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ALKYL LEAD ANTIKNOCK APPRECIATORS

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This invention is directed to new organic chloro compounds of the class of chloro-substituted hydrocarbylidene dialkanoates, which are useful petroleum chemicals. More particularly, this invention is directed to leaded high octane high aromatic content gasolines containing new organic chlorine compounds as antiknock boosters for the alkyl lead fuel component and as scavengers of lead products of combustion.

The advent of spark ignition engines of higher and higher compression ratios has demanded fuels of higher and higher resistance to knock. Improvements in the knock resistance of such fuels have been achieved through refining of hydrocarbon fractions, blending of fuel components and the use of antiknock agents. Hydrocarbons, unsuitable for gasoline use or of low octane number, are converted to high octane number stocks for gasoline use by refining methods. One refining method currently used is the catalytic cracking of higher petroleum fractions to gasoline fractions generally rich in olefins and aromatic hydrocarbons. Another refining method used is the catalytic reforming of low octane hydrocarbon fractions to high octane fractions of high aromatic content. Another refining method is the alkylation of olefins with paraffins to produce isoparaffins of branched structure and high octane number. These refinery stocks, as blends in various proportions, are employed in producing present day high quality commercial gasolines.

Because of economic and technical limitations to achieving fuel quality through refining and blending technics alone, tetraethyl lead has been widely employed to meet the demands for higher octane number gasolines. However, there are limitations to the use of tetraethyl lead. Fuels containing relatively large proportions of aromatic hydrocarbon components respond rather poorly (relative to paraffinic hydrocarbons) to the knock-suppressing potential of tetraethyl lead.

Recently it has been proposed to employ certain organic substances such as aldehydes, carboxylic acids, carboxylic anhydrides and carboxylic esters to improve the performance of organo lead antiknock agents in high aromatic content gasolines. Such proposed alkyl lead appreciators are halogen-free, since the introduction of halogen into such substances was observed to exert a marked depreciating effect on the antiknock quality of the fuel, as disclosed, for example, in Australian patent application 42,139/58. Such harmful tendency of halogen compounds on leaded fuel quality is suggested also by Livingston, "Antiknock Antagonists," Industrial and Engineering Chemistry, vol. 43, pages 663–664 (1951).

It is, therefore, an object of this invention to improve the response of motor fuel compositions, said compositions containing substantial amounts of aromatic hydrocarbons, to the knock-suppressing action of organo lead antiknock compounds.

It is also an object of the present invention to provide a novel class of chlorine containing organic compounds.

It is another object of the present invention to provide

novel gasoline compositions as hereinafter described and claimed.

More specifically, the present invention is directed to a novel class of organic chlorine containing compounds and to a motor fuel comprised of a mixture of hydrocarbons in the gasoline boiling range of which at least 15% by volume are aromatic hydrocarbons of the character of those occurring in catalytically cracked and reformed gasolines, and which mixture of hydrocarbons has an octane rating of at least 80 as measured by the ASTM Research Method (D–908–59), an antiknock quantity of a tetraalkyl lead antiknock compound and from about 0.2 to 1.5 theory of said novel compound, which compound is a chloro-substituted hydrocarbylidene dialkanoate of the formula,

$$R—CH(O—Ac)_2$$

where R is a chloro-substituted phenyl, alkyl or cycloalkyl radical having up to about 6 carbon atoms and having 1 to 2 Cl atoms and Ac is a lower-acyl radical containing up to 4 carbon atoms. The term chloro-substituted alkylidene radical will be used hereinafter to include those radicals where R is cycloaliphatic as well as aliphatic since the structure of these radicals does not appear to be critical for the purposes of this invention.

The herein described chloro-substituted alkylidene and benzylidene dialkanoates significantly improve the response of such mixtures of hydrocarbons to the antiknock activity of the organo lead antiknock compounds, although such chloro compounds exhibit no antiknock properties in and of themselves, that is, in the absence of the tetraalkyl lead component. These improvements in the antiknock performance of such leaded motor fuels, while normally not exceeding one octane number at the concentrations of additive contemplated, are significant in high octane number fuels because of the technical difficulty in and relatively high cost of achieving comparable increases by the use of more extensive fuel refining and blending techniques or by the use of additional quantities of organo lead antiknock agent. For example, the addition of a 4th ml. of tetraethyl lead per gallon of aromatic gasoline as heretofore described, and already containing 3 ml. of this antiknock agent per gallon, results in an improvement in the knock rating of about 1 octane number.

The comparative effectiveness of the novel chloro compounds utilized in the practice of the present invention is particularly surprising in view of the known antagonism towards alkyl lead antiknocks exhibited by halogen compounds.

The novel chloro compound component of this invention provides the additional benefit of functioning effectively as scavengers for lead in the fuel combustion products. Moreover, said chloro compounds function effectively as scavengers in the presence or absence of other organic halogen scavenging agents for lead.

The fuel utilized in the practice of this invention may be a commercial gasoline containing the aromatic hydrocarbons or it may be a blend of hydrocarbons of the character of those present in such gasolines. Thus, for example, it may be a catalytic-cracked stock, a catalytic-reformed stock, or blends of one or more of these cracked and reformed stocks, or blends of one or more of the above stocks with saturated stocks such as the synthetic alkylates and straight run stocks.

Typical aromatic hydrocarbons, which are essential components of the gasoline compositions of this invention and which are of the character of those aromatic hydrocarbons produced in catalytic cracking and catalytic reforming operations, are the mono- and poly- lower alkyl benzenes such as toluene, ethylbenzene, the xylenes and the trimethylbenzenes, diisopropylbenzene, and the like.

Typical catalytic-cracked refinery stocks which may be utilized contain from about 6 to 25 volume percent aromatics and about 29–44 volume percent olefinics, the rest being saturated hydrocarbons. Catalytic-reformed stocks run higher in aromatics, usually 40 to 70 volume percent, and are lower in olefins. Synthetic alkylates are essentially saturated hydrocarbons, high in isoparaffins. Refinery stock such as these are blended in various proportions for the production of commercial fuels for spark ignition internal combustion engines. These fuels normally boil within the range of about 80° F. to 440° F. Blended fuels for commercial use, such as those for automotive use, contain on the average from about 10 to 55 volume percent aromatic, up to about 30% olefinic, with the rest saturated hydrocarbons.

The motor fuels utilized in the practice of this invention contain at least 15 volume percent and normally not more than about 75 volume percent aromatic hydrocarbons. Olefinic hydrocarbons are not essential. Preferably, said fuels contain at least about 25 volume percent aromatics and less than 30 volume percent olefinics.

Preferably also, said fuels will be of high quality with respect to knock resistance, for example, they will have a Research Method octane rating of at least 80.

The motor fuels may also contain other additives normally associated with finished gasolines, such as antioxidants, metal deactivators, dyes, detergents, anti-icing agents, ignition control additives such as phosphorus compounds, and the like.

The organo lead antiknock agent employed may be any of those known to the art for such purposes, but usually will be a lower tetraalkyl lead, such as tetramethyl lead, tetraethyl lead, methyl triethyl lead, dimethyl diethyl lead, trimethyl ethyl lead, tetraisopropyl lead, and the like, and mixtures of any two or more such antiknock agents. The amount employed will usually provide 1 to 4 grams of Pb for each gallon of the fuel, preferably 2 to 3 grams per gallon.

The herein described chloro-substituted hydrocarbylidene dialkanoates are conveniently prepared by reacting chloro-substituted aldehydes with carboxylic acid anhydrides in the presence of a catalytic amount of a strong acid. For example by the method described by Man, Sanderson and Hauser, J. Am. Chem. Soc., 72, 847 (1950), o-chlorobenzylidene diacetate is obtained from o-chlorobenzaldehyde and acetic anhydride in the presence of a small amount of boron-trifluoride diethyl etherate. By this method there are readily obtained other chloro-substituted benzylidene dialkanoates as well as chloro-substituted alkylidene dialkanoates for use in this invention. For example, substituting such aldehydes as p-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, chloroacetaldehyde, 3-chloropropionaldehyde, and 2-methyl-2,3-dichlorobutyraldehyde for o-chlorobenzaldehyde in the above reaction yields p-chlorobenzylidene diacetate, 2,4-dichlorobenzylidene diacetate, 2-chloroethylidene diacetate, 3-chloropropylidene diacetate, and 2,3-dichloro-2-methylbutylidene diacetate. Similarly, 1-chlorocyclohexane-1-carboxaldehyde and 1,2-dichlorocyclopentane-1-carboxaldehyde may be employed in this method to yield diacetoxy (1-chlorocyclohexyl) methane and diacetoxy (1,2-dichlorocyclopentyl)methane, respectively. Similarly, the corresponding dipropionates and dibutanoates are prepared by employing propionic and butyric acid anhydride in place of acetic anhydride. Mixtures of aldehydes and mixtures of acid anhydrides may also be used to obtain mixtures of chloro-substituted hydrocarbylidene dialkanoates, useful as alkyl lead antiknock boosters.

In general, the chloro compounds derived from the aliphatic aldehydes tend to be liquid, those from the aromatic aldehydes solid. All are insoluble in water and soluble in hydrocarbon solvents. The novel fuel compositions of the present invention are prepared by dissolving the chloro-containing substance in the gasoline, before, after or simultaneously with the addition of the tetraalkyl lead antiknock agent.

The use concentration range of the chloro compounds of the present invention in gasoline is dependent on the ratio of the number of atoms of chlorine to the number of atoms of lead in the leaded gasoline. This dependency is logical since the chloro compounds do not affect the antiknock quality of the unleaded gasoline (i.e., the base fuel) in and of themselves but improve the response of the leaded gasoline. One theory of halogen is defined as the quantity theoretically required for reaction of the halogen with the lead to form the lead halide, which quantity is two atoms of halogen per atom of lead. Thus, the use concentration range of this invention as herein described is normally 0.2 to 1.5 theory of chlorine, that is the chloro compound is used in amounts providing 0.4 to 3 atoms of chlorine per atom of lead of the tetraalkyl lead antiknock agent. Preferably the use concentration range of the chloro compound furnishes about 0.5 to 1.0 theory (1 to 2 atoms of chlorine) per molecule of tetraalkyl lead.

It is common and conventional practice to incorporate into the motor fuel with the organo lead antiknock a compound which acts as a scavenger for lead in the combustion of the motor fuel in the engine. Such halohydrocarbon scavenging agents constitute a well known class of compounds and a great many have been disclosed in the art. However, it is usually preferred to employ ethylene dibromide or ethylene dichloride or a mixture thereof as the scavenging agent.

In the practice of this invention, the chloro-substituted hydrocarbylidene dialkanoates may be used alone as the sole scavenger or in combination with other known scavengers. Thus, there may be used 0.2 to 1.5 theories of chlorine as a chloro-substituted hydrocarbylidene dialkanoate in combination with up to about 2.0 theories of halogen as chloro- and bromo-containing hydrocarbons. Generally, the total halogen ranges from 1 to 2.5 theories with not more than about 0.5 theory being bromine. Preferably there will be employed 0.5 to 1.0 theory of the novel chloro compound and 0.5 to 1.5 theories of halogen as one or more ethylene dihalide, $X—CH_2—CH_2—Y$, wherein X and Y are Cl or Br and may be the same or different, with not more than 0.5 theory being bromine. The new compounds of this invention may be added to the conventional formulations such as Motor Mix (i.e., tetraalkyl lead fluids containing 0.5 theory of bromine as ethylene dibromide and 1 theory of chlorine as ethylene dichloride as further illustrated below) or they may replace part of the other halogen compounds to the extent of 0.2 to 1.5 theory halogen as defined.

In the examples described below, fuel composition, in terms of hydrocarbon content, is in volume percent. Fuels described as having been leaded to contain tetraethyl lead were leaded by incorporating therein Motor Mix having the following composition, in percent by weight: tetraethyl lead, 61.4%; ethylene dibromide, 17.86% (0.5 theory Br); ethylene dichloride, 18.81% (1.0 theory); an orange dye, 0.05%; and inert solvent oil, 1.88%. Fuel quality, the resistance of the fuel to knock, is determined by the standard ASTM Research Method. The concentrations below refer to the alkyl lead component.

Representative examples illustrating the present invention follow:

Example 1

A. p-Chlorobenzylidene diacetate is prepared from the ingredients tabulated below, according to the method of Man, Sanderson and Hauser mentioned above.

	Mole	Gram	Ml.
p-Chlorobenzaldehyde	0.50	70	
Acetic anhydride	0.75	77	
Boron trifluoride diethyletherate			1
Diethyl ether anhydrous			50

The aldehyde is added dropwise over a 2.5 hour period to a solution of acetic anhydride in ether maintained at 0–5° C. under an anhydrous atmosphere. The reaction mixture is stirred for 1.5 hours longer, drowned in 400 ml. of 10% weight aqueous sodium acetate and filtered to obtain crystalline product. An additional quantity of the diacetate is recovered from the ether by evaporation providing a total of 115 grams, melting range 85–87° C.

B. The chloro-substituted hydrocarbylidene diacetates tabulated below are prepared from the appropriate aldehydes following essentially the same procedure described under "A":

2,4-dichlorobenzylidene diacetate, M.P. 98–110° C.;
o-Chlorobenzylidene diacetate, M.P. 50–52° C.;
2-methyl-2,3-dichlorobutylidene diacetate, B.P. 129–132° C. at 10 mm. of Hg pressure;
3-chloropropylidene diacetate, B.P. 125–130° C. at 15 mm. of Hg pressure.

The utility of the novel compounds of the present invention in gasoline is illustrated in the following examples.

Example 2

A commercial premium grade leaded gasoline having a Research octane rating of 102.1, containing 3.0 ml. TEL/gal. as Motor Mix, and analyzing 48% aromatics, 13% olefins, and 39% saturates is treated to contain 2 gr./gal.=0.25 theory of chlorine as 3-chloropropylidene diacetate, thereby increasing the octane rating of the fuel 0.2 octane number.

Similarly with 2-methyl-2,3-dichlorobutylidene diacetate at a concentration of 1 gr./gal. providing 0.25 theory chlorine the Research octane rating of the above premium leaded gasoline is improved 0.2 octane number to 102.3.

Example 3

A catalytic reformate gasoline, consisting of 52% aromatics, 3% olefins and 45% saturates, is leaded with Motor Mix to contain 3 gr. of Pb/gallon and to have a Research octane rating of 101.1. To this fuel is added a chloro-substituted benzylidene diacetate to increase the octane rating as tabulated below.

Chloro Compound	Concentration		Increase in Research Octane Number
	Gr./gal.	Theory Cl	
p-$ClC_6H_4CH(OAc)_2$	6	0.8	0.3
o-$ClC_6H_4CH(OAc)_2$	3	0.4	0.2
2,4-$Cl_2C_6H_4CH(OAc)_2$	3	0.7	0.3
2,4-$Cl_2C_6H_4CH(OAc)_2$	6	1.4	0.3

3-chloropropylidene diacetate used in place of the above benzylidene compounds at a concentration of

3 gr./gal.=0.5 theory

in the same leaded gasoline increases the octane rating to 101.5.

Example 4

A tetraalkyl lead mixture having the composition 6.25 mole percent tetraethyl lead, 25 mole percent triethyl methyl lead, 37.5 mole percent dimethyldiethyl lead, 25 mole percent trimethyl ethyl lead, and 6.25 mole percent tetramethyl lead is dissolved along with 1.0 theory of chlorine as ethylene dichloride in a premium gasoline base stock consisting of 34% aromatics, 23% olefins, and 43% saturates. The resulting leaded fuel has a Research octane rating of 98.4. The addition to this fuel of 0.5 theory of chlorine as 2,3-dichloro-2-methylbutylidene diacetate improves the octane rating by 0.3 octane number.

In contrast to the effectiveness of the chloro-alkylidene and chloro-benzylidene dialkanonates shown in the preceding representative examples to improve the antiknock quality of leaded high aromatic content gasoline, the conventional halohydrocarbon scavenging agents for lead, such as the ethylene dihalides of the commercial tetraalkyl lead antiknock mixes, do not function as tetraalkyl lead antiknock appreciators in the described compositions.

It is understood that the preceding examples are repsentative and that they may be varied within the scope of the total specification disclosure, as understood and practiced by one skilled in the art, to achieve essentially the same results.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Motor fuel compositions comprising a mixture of hydrocarbons in the gasoline boiling range having at least 15% by volume aromatic hydrocarbons, which mixture of hydrocarbons has an octane rating of at least 80, an antiknock quantity of tetraalkyl lead compound and from 0.2 to 1.5 theories of chlorine as a chloro-substituted hydrocarbylidene dialkanoate of the formula

$$R—CH(O—Ac)_2$$

where R is a chloro-substituted radical selected from the group consisting of phenyl, alkyl and cyclo-alkyl, said radical having up to and including 6 carbon atoms and having 1 to 2 chlorine atoms, and wherein Ac is a lower-acyl radical containing up to and including 4 carbon atoms.

2. A composition according to claim **1** wherein R is phenyl.

3. A composition according to claim **1** wherein R is alkyl.

4. A composition according to claim **1** wherein said dialkanoate is 2-methyl-2,3-dichlorobutylidene diacetate.

5. Motor fuel compositions comprising a mixture of hydrocarbons in the gasoline boiling range having at least 25% by volume aromatics and not more than 30% by volume olefinics, which mixture of hydrocarbons has an octane rating of at least 80, an antiknock quantity of tetraalkyl lead compound, and from 0.5 to 1.0 theory of chlorine as a chloro-substituted hydrocarbylidene dialkanoate of the formula

$$R—CH(O—Ac)_2$$

wherein R is a chloro-substituted radical selected from the group consisting of phenyl, alkyl and cycloalkyl, said radical having up to and including 6 carbon atoms and having 1 to 2 chlorine atoms, and wherein Ac is a lower-acyl radical containing up to and including 4 carbon atoms.

6. Motor fuel compositions comprising a mixture of hydrocarbons in the gasoline boiling range having at least 15% by volume aromatics, which mixture of hydrocarbons has an octane rating of at least 80, an antiknock quantity of tetraalkyl lead compound, from 0.2 to 1.5 theories of chlorine as a chloro-substituted hydrocarbylidene dialkanoate of the formula

$$R—CH(O—Ac)_2$$

wherein R is a chloro-substituted radical selected from the group consisting of phenyl, alkyl and cycloalkyl, said radical having up to and including 6 carbon atoms and having 1 to 2 chlorine atoms, and wherein Ac is

a lower-acyl radical containing up to and including 4 carbon atoms, and from 0.5 to 1.5 theories of halogen as ethylene dihalide of the formula

$$X—CH_2CH_2—Y$$

wherein X and Y are each selected from the group consisting of chlorine and bromine, with the proviso that not more than 0.5 theory of said halogen is bromine.

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