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ANTIKNOCK MOTOR FUEL

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10 Claims. (Cl. 44—63)

This invention relates to gasoline-type motor fuels, i. e., motor fuels suitable for use in gasoline engines, and more particularly deals with gasoline type motor fuels of high anti-knock properties containing metal-organic knock suppressors.

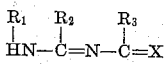
As is well-known, certain mineral oil-soluble metal-organic compounds such as tetraethyl lead, nickel and iron carbonyls, ethyl selenide, etc., have the property of suppressing detonation or knock in spark ignition engines. These compounds are generally known as anti-knock compounds. While some of them are highly effective, they are all subject to at least one or several serious disadvantages, such as insufficient solubility in hydrocarbons, low volatility, high toxicity, poor storage stability, corrosiveness to the engine, etc.

It is a purpose of this invention to provide a class of efficient knock suppressors comprising metal-organic compounds which are substantially free from the above disadvantages or at least to possess them to a very much smaller extent. It is another purpose to provide non-toxic anti-knock compounds readily soluble in gasoline having efficiencies comparable to those of tetraethyl lead.

I have discovered that members of a certain class of metal-organic compounds are particularly effective as anti-knock agents because of their properties of an anti-knock value comparable with that of lead tetraethyl, low toxicity, good volatility and high solubility in gasoline. In particular, the solubility in gasoline of these compounds is generally very high, many members being miscible with gasoline in all proportions.

My anti-knock agents are compounds of a metal having an atomic number of 26 to 29 inclusive, i. e. a metal selected from the class consisting of iron, cobalt, nickel and copper and an organic substance containing the atom combination N—C—N—C—O or N—C—N—C—N, this combination containing at least 2 double bonds each of which may be between two atoms of the chain, or between an atom of the chain, and a radical outside of the chain. The metal is probably bound either to a nitrogen or an oxygen atom or both.

Particularly useful are metal compounds of substances with the following basic structure:



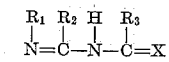
in which X=O or NR_4 and R_1, R_2, R_3 and R_4 represent hydrogen atoms or organic radicals selected from the group consisting of alkyl, aryl or aralkyl which may or may not contain one substituent.

Suitable substituents in hydrocarbon radicals R_1 to R_4 are all those which are capable of forming substantially stable compounds with the hydrocarbons, such as halogen, —CN, —OH, —OR, —COR, —NH_2, —NHR, —NR_2, —SH, —SR, —COOR, etc., where R is an alkyl, aryl or aralkyl radical and the subscript two of group —NR_2 refers to a plurality of R radicals, neutral and basic substituents being preferred to those which are strongly acidic, such as —COOH, —SO_3H, etc. Furthermore, both N—C—N—C—N and

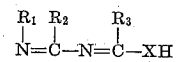
N—C—N—C—O

groupings may partially occur in a ring system in which at least two of the atoms contained in the groupings participate as in the case of 2 or 3 amino-imidazoles, and acetylated alpha pyridines, while the N—C—N—C—N grouping may occur wholly in a ring system as is the case with 1,2,4 triazoles.

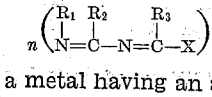
As is well known in compounds of the above formula, the double bonds are capable of shifting their exact location within the molecule depending upon the surrounding conditions, thereby forming the enol and keto forms and amino or imino forms, respectively. Therefore the following structures are considered full equivalents of the above.



and



The metal compounds of my invention may be conceived as salts or complex compounds or both. It is believed that the metal is usually attached to the oxygen, or to one of the nitrogen atoms, by replacement of a hydrogen atom as follows:

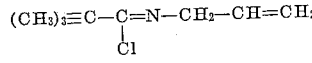


where Me is a metal having an atomic number of 26 to 29 and n is the valence of the metal, X being oxygen or NR_4. It is likely that in addition there are links of secondary valences between the metal and at least one of the other nitrogen atoms.

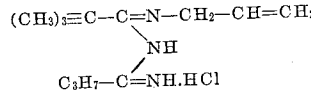
The compounds which I add to gasoline according to this invention and their methods of preparation have been described in my co-pend-

ing Patent 2,196,447. An example of a typical method of preparation is as follows:

About 15.5 parts by weight of pivalyl-allyl-imide chloride



which may be prepared by reacting pivalyl chloride with allyl amine and treating the resulting pivalyl-allyl-amide with phosphorus pentachloride to form pivalyl-allyl- amide chloride which loses HCl spontaneously giving the desired pivalyl-allyl imide chloride, were dissolved in about 15 parts by weight of benzene. This solution was added slowly to a cooled solution consisting of about 8 parts by weight of butyramidine dissolved in about 12 parts by weight of benzene. After the addition of the reactants was complete, the reaction was completed by heating the mixture to a temperature of about 80° C. for about one hour. The benzene was removed by evaporation. The residue was dissolved in methyl ethyl ketone, and the product recovered in a purified form by crystallization therefrom. Analysis of the product showed it to have the structural formula



This novel compound may be designated as (allyl-pivalo) butyr-imidine hydrochloride.

The metal derivative of the compounds may be prepared by reacting them with suitable compounds of the desired metal. Thus, for example, sodium compounds may be prepared by reaction with sodium ethylate. The corresponding copper cobalt iron or nickel compounds may be prepared by reacting suitable compounds of these metals with the sodium derivatives of the desired organic component, in an absolute alcohol solution. Further examples may be found in my co-pending application, Serial No. 217,278, filed July 2, 1938.

If desired, gasoline type motor fuels may be prepared consisting entirely or predominantly of neutral oxyhydrocarbons, such as ethers, ketones, or alcohols, particularly those with branched carbon chains, and boiling within gasoline range, containing small amounts of our anti-knock compounds. Such oxyhydrocarbons also may increase the solubility in hydrocarbons of certain of my anti-knock compounds which are relatively little soluble.

The amounts of my anti-knock compounds normally incorporated into the fuels to effect an improvement in the knock rating may vary from a bare trace to about .5% metal by weight of the fuel, although larger amounts may be used, if desired. Moreover, my anti-knock compounds may be used together with other known anti-knock compounds such as tetraethyl lead. If necessary my anti-knock compounds may be stabilized by the addition of suitable stabilizing agents of which the aromatic amines are particularly effective.

Of the four metals, iron, nickel, cobalt and copper found to possess the high anti-knock properties when combined with the organic compounds described, copper and cobalt are the most outstanding and effective.

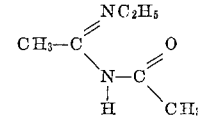
Examples of types of suitable compounds are the copper, cobalt, nickel and iron compounds of the following:

Containing the N—C—N—C—N grouping	Containing the N—C—N—C—O grouping
Imidines	Acetylated amidines
2 or 4—amino pyrimidines	Acetylated alpha aminopyridines
1,2,4 triazoles	Acetylated iso-ureas
2 or 3—amino imidazoles	Acetylated guanidines

The following examples illustrate the manner in which these compounds may be used, and the highly satisfactory results obtained.

Example I

To a gasoline with an octane number of 40, 0.1% by weight of copper was added in the form of the cupric compound of acetyl ethyl acetamidine



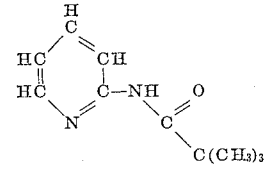
As a result the octane number rose to 59.

Example II

0.1% by weight of copper in the form of the cupric compound of propionyl methyl acetamidine raised the octane number of a gasoline from 40 to 61.5.

Example III

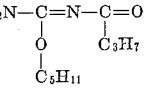
0.1% by weight of copper in the form of the cupric compound of alpha (pivalyl amino) pyridine.



raised the octane number of a gasoline from 40 to 50.

Example IV

0.1% by weight of copper in the form of the cupric compound of butyryl isoamyl iso-urea

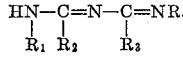


raised the octane number of a gasoline from 39 to 46.

I claim as my invention:

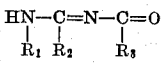
1. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock suppressor comprising a compound combining a metal having an atomic number from 26 to 29 inclusive, with an organic component, having a basic structure which contains an atom combination selected from the group consisting of N=C—N—C=O and N=C—N—C=N or their tautomers, the structure containing at least two double bonds.

2. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock-suppressor comprising a compound of a metal having an atomic number from 26 to 29 inclusive, and an organic component having a structure represented by the formula



and its tautomers in which R_1–R_4 are radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals.

3. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock-suppressor comprising a compound of a metal having an atomic number from 26 to 29 inclusive, and an organic component having a structure represented by the formula



and its tautomers in which R_1–R_3 are radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals.

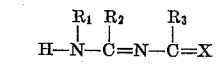
4. The improved motor fuel of claim 1, the organic component of which forms a ring in which at least two of the atoms of such structure participate.

5. The improved motor fuel of claim 1, which contains not more than .5% metal by weight of the motor fuel.

6. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of the cupric compound of propionyl methyl acetamidine.

7. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of the cupric compound of α(pivalyl amino) pyridine.

8. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock suppressor comprising a compound combining a metal having an atomic number from 26 to 29 inclusive, with an organic component having a basic structure which contains an atom combination



or its tautomeric equivalents, where X is a radical selected from the group consisting of oxygen and imino radicals, and R_1 to R_3 are radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals.

9. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock suppressor in excess of its solubility in the fuel, comprising a compound combining a metal having an atomic number from 26 to 29 inclusive, with an organic component having a basic structure which contains an atom combination selected from the group consisting of N=C—N—C=O and N=C—N—C=N or their tautomers, the structure containing at least two double bonds, and a quantity of a mutual solvent soluble in the fuel boiling within the gasoline boiling range, selected from the group consisting of alcohols, ketones, ethers and amines, sufficient completely to dissolve the knock suppressor.

10. An improved motor fuel which comprises a gasoline type motor fuel and a small amount of a knock suppressor in excess of its solubility in the fuel, comprising a compound combining a metal having an atomic number from 26 to 29 inclusive, with an organic component having a basic structure which contains an atom combination selected from the group consisting of N=C—N—C=O and N=C—N—C=N or their tautomers, the structure containing at least two double bonds and stabilized by the addition of small quantities of aromatic amines.

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