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MOTOR FUEL

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11 Claims. (Cl. 44—9)

This invention relates in general to improved motor fuels, and pertains more specifically to the improvement in motor fuels which resides in the addition thereto of selenium compounds which impart to the fuel anti-detonating properties.

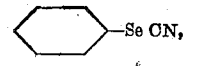
In the gasolines and other hydrocarbon fuels made according to present methods of production, there is a tendency to produce fuels which contain constituents of a nature giving a low compression value to the fuel. In gasolines used in automobiles, the compression ratio of the gasoline in itself is ordinarily much lower than that which is desired for the proper operation of the motor. The use of low compression fuels is accompanied by a "knocking" or detonation of the fuel under conditions which are met with very frequently during normal operation. It has been customary to add substances to the motor fuels of this type which will increase the compression value of the fuel, effecting a diminuation or a complete elimination of this "knocking" characteristic. Many of these anti-detonating agents give a satisfactory high compression ratio to the gasoline. However, they are in general rather expensive, and may of them are unsatisfactory for commercial use due to the great expense incurred in adding them to the fuel. Furthermore, in the use of certain well-known anti-knock agents, undesirable deposits are formed during the operation of the motor which, over an extended period of time, result in a lowering of the efficiency, and interference with the smooth and proper running of the engine. Other anti-knock agents are unsatisfactory due to the evolution of poisonous fumes resulting from combustion, or on account of the generation of vapors having an unbearable odor.

Our invention has for its object the production of motor fuels which are highly desirable for use in automobiles. The invention contemplates the addition to low compression fuels of substances which will add considerably to the highest useful compression ratio of the fuel without the disadvantages which result from the use of the anti-knock agents now on the market.

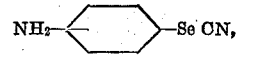
Our invention deals more particularly with the use of selenium compounds as anti-detonating agents in gasolines, and particularly embraces the use of diselenide compounds for this purpose. In addition to the diselenide compounds, we contemplate as efficient anti-knock agents the use of many compounds containing a seleno cyanate group (—Se—C N), the term "cyanate" being designed to include also "isocyanate". This interpretation of the term will be adhered to throughout the specification and claims. Similarly, the term "nitrile" wherever used will include the isomer, "isonitrile" and the groups —C N or N C— will be meant to illustrate both nitrile and isonitrile.

Selenium compounds have generally been suggested for use in the art as anti-knock agents. The selenium compounds heretofore used, however, have the disadvantage that their efficiency as anti-detonating agents does not compare sufficiently favorably with the more commonly used anti-knock compounds to make them adaptable for general use. Moreover, the selenium compounds heretofore suggested by the art impart a very objectionable odor to the gasolines in which they are incorporated.

We have discovered in the course of our experimentation that the group —Se—C N, or selenocyanate, in itself contributes very decided anti-detonating properties to the compounds of which it is a radical. This distinctive radical may be coupled up with organic or inorganic residues of widely varying character. Many compounds of this general type have been prepared and tested with highly satisfactory results. Among the more effective compounds of this type, we have found

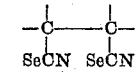


phenyl selenocyanate, and its amino substituted derivative

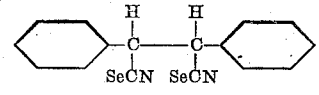


which may be further alkylated to give alkyl secondary or tertiary amino derivatives. Aliphatic seleno cyanates and their derivatives, and other forms of organic seleno cyanates are satisfactory anti-knock agents. Also seleno cyanates containing inorganic substituent radicals have similar properties.

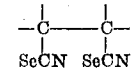
Compounds containing the following nucleus



such as



and aryl amine substituted derivatives also contain similar properties which are accentuated to a certain extent by the introduction of the amino group. Here also, as in the case of the compound having a single —Se C N linkage, aliphatic or other types of organic substituent radicals, or inorganic radicals may be joined to the



group with the production of anti-knock compounds.

We have found, further, that where compounds of the type of diselenides, namely substances having the group —Se—Se—, are introduced into motor fuels, they result in a raising of the compression value of the fuel in an amount greatly in excess over that possessed where the selenium compounds heretofore known to the art have been used.

The diselenide compounds are found generally to be solid, crystalline compounds which are substantially non-volatile, being thereby distinguished from the monoselenides, which are liquid and are relatively quite volatile. In stating that the diselenides are non-volatile, it is meant that their degree of volatility is markedly less than that of the least volatile hydrocarbon constituents of the fuel. Some of the aliphatic diselenides are normally liquid, but these compounds too are non-volatile within the meaning of the definition above given for the term. These diselenide compounds are comparatively inexpensive, easily available, generate no poisonous or obnoxious fumes which would interfere with the operator, and do not cause the deposition of solid products of combustion which would in any way interfere with the proper functioning of the motor. They furthermore possess anti-knock characteristics many times in excess of those possessed by the selenium compounds known to the art heretofore.

The diselenide derivatives have been found to be very soluble in gasoline, which is a property necessary for commercial adaptability of an anti-knock compound. Furthermore, the diselenides have the very desirable feature of being non-reactive with relation to the gasoline into which they are introduced. The effect of the diselenide will, therefore, be substantially independent of the type of gasoline with which it is used. The absence of this feature from many anti-knock "dopes" have lessened their usefulness to a great degree, such "dopes" being unreliable for the purpose of obtaining standard anti-detonating effects from the introduction of a standard amount of compound into a gasoline fuel. With the diselenide compounds of our invention, however, we have found that these compounds are quite stable, and that regardless of the particular type of fuel with which the compound is used, the same anti-detonating value may be evidenced where standard amounts of the material are used.

Another valuable feature accompanying the use of diselenide compounds is their property of imparting to hydrocarbon solutions of the same a characteristic golden yellow tint. This property is highly desirable for the purpose of identifying gasolines.

We have found that diselenide compounds contain high anti-knock characteristics independently of the type of substituent groups which are attached to the selenium atoms. It appears to be essential to the efficacy of the compounds merely to have present the distinctive diselenide grouping, in which one atom of selenium is attached to another. The diselenide compounds may have attached to the selenium atoms inorganic radicals. These inorganic radicals may be identical for each selenium atom. However, this is not necessary, a wide range of variation between the substituent groups attached to the selenium atoms being possible. In this connection, we have found also that further selenium groups may, if desired, be attached directly to the diselenide linkage for the purpose of forming polyselenides having more than two selenium atoms in the chain.

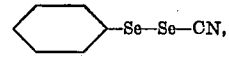
The radicals attached to the selenium atoms may be organic radicals in lieu of the inorganic radicals above mentioned. These organic radicals attached to the selenium atoms may be either aromatic or aliphatic. The nature of the radical may vary considerably. For example, the aliphatic radicals may be straight chain hydrocarbon residues or may be branched chains of the type of the isohydrocarbon radicals. They may be saturated or unsaturated aliphatic radicals. They may vary in the number of carbon atoms in the radical within wide limits. The aromatic nuclei attached to the selenium atoms may be mononuclear or polynuclear, and they may be further substituted by additional aromatic or aliphatic groupings. The aliphatic residues likewise may contain, substituted therein, aromatic hydrocarbon radicals. The hydrocarbon radicals attached to the selenium atoms may be further substituted by non-hydrocarbon substituents, if desired. For example, it has been found very desirable to introduce amino groups into the hydrocarbon radicals which are attached to the distinctive diselenide nucleus. Other groups which may be substituted are nitrile, isonitrile, hydrazo, and in general the usual substitutions may be made depending upon the particular characteristics which the anti-knock compound is to possess.

Referring to the diselenides which contain inorganic radicals attached to their nuclei, we have found the following compounds to be very effective: NC—Se—Se—Se—CN and NC—Se—Se—CN. These specific compounds merely exemplify the utility of the broad class of inorganic diselenides.

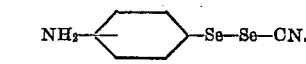
Many other inorganic substituted diselenides give highly satisfactory results when incorporated in a motor fuel, the cyanogen substituted compounds being taken merely as illustrative of a preferred form of compounds coming within this general class. For example, diamino diselenide (NH_2—Se—Se—NH_2), and the N-hydrocarbon substituted derivatives of the same, raise the compression value of hydrocarbon motor fuels. Diselenides substituted generally by inorganic substituents will be found highly desirable for the purposes of the invention.

The invention embraces also the use of diselenides having an inorganic radical attached to one selenium atom and an organic residue, substituted or unsubstituted, attached to the other selenium atom in the group. Compounds of this type will correspond to the formula: R—Se—Se—R_1, where R represents an organic radical. Preferred substances coming under this class are of the following types:

C_2H_5—Se—Se—CN, in which the ethyl radical may be other alkyl or substituted alkyl radicals,



in which the phenyl radical may be any other aryl group, which in turn may be further substituted by organic or inorganic groups; amine substituted compounds of this general type may be exemplified by the following:



Where the diselenide group is linked up with a nitrile or isonitrile group, unusual efficiency as anti-knock agents is imparted to this class of compounds, due not only to the diselenide linkage but also to the selenocyanate relationship in the compounds. The two compounds, namely, seleno selenium cyanate and dicyan diselenide already specifically mentioned, represent preferred compounds for use according to our invention having anti-detonating values far in excess over those possessed by any selenium compounds which have been heretofore used in connection with motor fuels. These compounds are, furthermore soluble in gasoline, imparting to it the characteristic diselenide color effect. We have found that where the selenium seleno cyanate is dissolved in gasoline, there is a tendency for the compound to break down into the dicyan diselenide. However, the efficiency of the compound is not limited to its derivative, since the selenium seleno cyanate itself possesses very desirable anti-knock properties.

Mention has already been made of the fact that the diselenide group is chromophoric and imparts a distinctive golden yellow tint to gasoline. This color intensity is enormously increased by the attachment to the diselenide group of amine groups, particularly of the anilino or substituted anilino type.

The following example illustrates the adaptation of one of the preferred forms of my invention:—

The compound Se_3CN_2 is formed by the action of oxides of nitrogen on potassium seleno-cyanate; and this compound dissolved in gasoline or in gasoline-benzol blends we have found to have a high anti-knock value. Weight for weight its anti-knock effect is of the same order of magnitude as lead tetra-ethyl.

As this compound has only a limited solubility in gasoline, we have found it desirable to use an auxiliary solvent. Cyclohexanol has been found particularly useful in this respect as a small amount thereof, added to the gasoline, increases the solubility of the selenium compound considerably.

This is merely illustrative of the general purpose and utility of the invention.

The specific compounds already referred to are capable of considerable change in structure while still retaining the highly desirable properties which are ascribed to them. Elements other than selenium may be introduced into the compounds, for example, iron and other metals may be attached to the selenium atoms, the derivative compounds being suitable for use in motor fuels. The modifications which may be made in the above compounds are embraced within the concept of the invention.

Numerous compounds of the above described classes have been tested and have uniformly been found to possess advantages far superior to those possessed by any selenium compounds used prior to this invention. Their additional advantages, namely, color characteristics, and far greater anti-detonating properties, adapt them for commercial use to an extent not heretofore found possible with any of the selenium compounds with which the art is familiar.

Tellurium compounds corresponding in general to the selenium compounds already mentioned, and derivates of the diselenides which have been referred to in which one selenium atom has been displaced by a tellurium atom, likewise possess anti-knock properties and are embraced within the scope of the invention.

We claim:—

1. A liquid motor fuel containing a compound having a seleno cyanate radical, which imparts a high compression value to the fuel.

2. A liquid motor fuel containing an organo derivative of a seleno cyanate which imparts a high compression value to the fuel.

3. A liquid motor fuel containing a hydrocarbon substituted derivative of a seleno cyanate, which imparts a high compression value to the fuel.

4. A liquid motor fuel containing an amino substituted hydrocarbon derivative of seleno cyanate, which imparts a high compression value to the fuel.

5. A liquid motor fuel containing an aliphatic derivative of a seleno cyanate which imparts a high compression value to the fuel.

6. A liquid motor fuel containing an amino substituted aliphatic derivative of a seleno cyanate which imparts a high compression value to the fuel.

7. A liquid motor fuel containing an aromatic derivative of seleno cyanate which imparts a high compression value to the fuel.

8. A liquid motor fuel containing an amino substituted aromatic derivative of a seleno cyanate which imparts a high compression value to the fuel.

9. A liquid motor fuel containing an anilino seleno cyanate, which imparts to the fuel a high compression value.

10. A high compression liquid motor fuel comprising hydrocarbon, to which has been added a compound corresponding to the formula R—Se—Se—CN, in which R represents a radical containing a cyanide group, the compound imparting to the hydrocarbon anti-detonating properties.

11. A high compression liquid motor fuel comprising hydrocarbon, in which has been incorporated dicyan diselenide.

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