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MOTOR FUEL

William M. Sweeney, Hopewell Junction, and Robert Y. Heisler, Fishkill, N.Y., assignors to Texaco Inc., a corporation of Delaware

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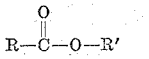
9 Claims. (Cl. 44—68)

This invention relates to an improved fuel composition containing a novel class of anti-knock agents for motor fuel.

This invention particularly concerns motor fuel anti-knock additives comprising the reaction products of acetylenic alcohol or its esters and dicobalt octacarbonyl. Moreover, we contemplate the addition of about 0.4 gram per gallon and up to the limit of solubility of these reaction products to a motor fuel to form a fuel composition of improved anti-knock rating. However, the preferred amount of additive is from 3 to 5 grams per gallon of motor fuel.

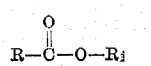
In general, acetylenic alcohols having from 3 to 20 carbon atoms are useful in the formation of these products, however, we prefer those having from 3 to 12. Some of the preferred acetylenic alcohols which are used, either as alcohols or in the form of their esters, to form the reaction products of the present invention are 2-propyn-1-ol, better known as propargyl alcohol, 2-methyl-3-butyn-2-ol, 3-methyl - 1 - pentyn-3-ol, 2,5-dimethyl-3-hexyn-2,5-diol, 3,6-dimethyl - 4 - octyn-3,6-diol and 1-ethynylcyclohexanol.

The esters which are useful in this invention are substituted or unsubstituted esters of acetylenic alcohols having the following general formula



wherein R is an alkyl or aryl radical which may or may not be substituted with a halogen, a nitro group or an —OR″, R′ is an aliphatic, hydroxy substituted aliphatic or cycloaliphatic radical containing at least one acetylenic bond and R″ is an aliphatic radical. The following are examples of such esters: propargyl acetate, propargyl trichloroacetate, propargyl trifluoroacetate, propargyl trichloroacrylate, propargyl benzoate, propargyl p-nitrobenzoate, propargyl 3,5-dinitrobenzoate, propargyl o-methoxybenzoate, propargyl m-bromobenzoate, propargyl o-iodobenzoate, propargyl o-chlorobenzoate, 1,1-dimethyl-2-propynyl trichloroacrylate, 1,1-dimethyl-2-propynl acetate, 1,1-dimethyl-2-propynyl p-nitrobenzoate, 1-methyl-1-ethyl-2-propynyl acetate, 1,1,4-trimethyl-4-hydroxy-2-pentynyl monotrichloroacrylate, 1,1,4,4 - tetramethyl-2-butynylene di-o-methoxybenzoate, 1,4-dimethyl-1-ethyl-4-hydroxy-2-hexynyl monoacetate, 1,4-dimethyl-1,4-diethyl-2-butynylene dibenzoate, 1-ethynylcyclohexyl acetate, 1-ethynylcyclohexyl trichloroacrylate, 1 - ethynylcyclohexyl m-bromobenzoate and 1-ethynylcyclohexyl - 3,5 - dinitrobenzoate. Where the esters of the present invention are formed with aliphatic acid portions, the acid portions contain from 1 to 20 carbon atoms but preferably from 1 to 6. Those halogenated aliphatic acid portions of the esters having from 1 to 6 carbon atoms are preferably fully halogenated.

Some of the preceding esters which have the general formula



where R represents an alkyl or aryl radical containing at least one halogen atom and R′ is an aliphatic, hydroxy substituted aliphatic or cycloaliphatic radical having at least one acetylenic bond are novel compounds and are disclosed as such in our copending application, Serial No. 514,117, filed of even date herewith and now abandoned.

In the formation of the compounds of this invention, two moles of carbon monoxide are given off in accordance with the following equation using propargyl alcohol for an example

$$HC{\equiv}C{-}CH_2OH + Co_2(CO)_8 \rightarrow HC{\equiv}C{-}CH_2OH{\cdot}Co_2(CO)_6 + 2CO\uparrow$$

It can be seen that a reaction product which might be termed propargyl alcohol dicobalt hexacarbonyl is formed along with the two moles of carbon monoxide.

It is recognized that metal carbonyls have been used as fuel additives. However, the cobalt carbonyl reaction products of this invention are more stable than cobalt carbonyl per se and do not require storage in an atmosphere of carbon monoxide as does cobalt carbonyl.

The reaction products of this invention, with the exception of that formed with propargyl alcohol are novel compounds and methods of forming them are presented in the following examples.

EXAMPLE 1

Preparation of propargyl trichloroacrylate dicobalt hexacarbonyl

10.6 g. of propargyl trichloroacrylate, 17.1 g. of dicobalt octacarbonyl and 250 cc. of pentane were mixed together and allowed to stand until the evolution of carbon monoxide ceased (3 hours). The mixture was filtered, solvent stripped, and a red crystalline residue crystallized from ethanol. Yield: 15 g., 60%.

The melting point of the product was 64 to 65° C. On analysis, the percentage composition was found to be as follows: C=29.3, H=0.8, Cl=21.9, Co=23.5, the molecular weight=471. The preceding values compare well with the theoretical values for the constituents of this compound which are C=28.8, H=0.6, Cl=21.5, Co=23.8 and the molecular weight=500. This reaction product exhibited excellent stability on standing in open air.

EXAMPLE 2

Preparation of propargyl p-nitrobenzoate dicobalt hexacarbonyl

12.6 g. of propargyl p-nitrobenzoate, 17.1 g. of dicobalt octacarbonyl and 250 cc. of pentane were allowed to stand until the evolution of carbon monoxide ceased (3 hours). The product was filtered and the precipitate recrystallized from benzene. Yield: 12 g., 48%.

The melting point was found to be 133 to 134° C. On analysis, the percentage composition was as follows: C=39.3, H=1.5, N=2.8, Co=23.2, the molecular weight=492. These values correspond closely to the theoretical composition which is C=39.0, H=1.4, N=2.7, Co=23.2 and the molecular weight is 492. This product also showed excellent stability on standing in open air.

EXAMPLE 3

Preparation of propargyl benzoate dicobalt hexacarbonyl

3.4 g. of dicobalt octacarbonyl, 1.7 g. of propargyl benzoate and 20 cc. of octane were mixed together and allowed to stand until the evolution of carbon monoxide ceased (1 hour). The mixture was filtered and the filtrate was stripped of the solvent under reduced pressure. The red crystalline material was recrystallized from water-ethanol mixture. Yield: 4 g., 93%.

The melting point of this additive was found to be

89 to 90° C. Analysis of the composition showed C=43.1, H=2.0, Co=26.7, the molecular weight=438. Again these figures closely coincide with the theoretical values which are as follows: C=43.2, H=1.8, Co=26.5 and the molecular weight is 446. No decomposition was observed on standing in open air.

EXAMPLE 4

Preparation of propargyl 3,5-dinitrobenzoate dicobalt hexacarbonyl

10 g. of propargyl 3,5-dinitrobenzoate, 13.7 g. of dicobalt octacarbonyl, 100 cc. of pentane and 50 cc. of benzene were allowed to stand until evolution of carbon monoxide ceased (3 hours). The solvents were removed and the red crystalline residue recrystallized from ethanol. Yield: 199 g., 87.5%.

The melting point was found to be 102° C. No decomposition of the compound was observed on standing in open air.

EXAMPLE 5

Preparation of propargyl acetate dicobalt hexacarbonyl

40 g. of propargyl acetate, 140 g. of dicobalt octacarbonyl and 300 cc. of pentane were mixed together and allowed to stand overnight. The product was filtered and the solvent was allowed to evaporate yielding a violet amorphous solid. Yield: 38 g., 25%.

This compound exhibited excellent stability on standing in open air.

EXAMPLE 6

Preparation of propargyl trichloroacetate dicobalt hexacarbonyl

42.8 g. of dicobalt octacarbonyl, 20.2 g. of propargyl trichloroacetate and pentane as required were mixed together and allowed to stand until the carbon monoxide elimination was completed. The product was filtered and the solvent was allowed to evaporate. A reddish crystalline substance was observed.

EXAMPLE 7

Preparation of propargyl trifluoroacetate dicobalt hexacarbonyl

42.8 g. of dicobalt octacarbonyl, 15.4 g. of propargyl trifluoroacetate and pentane as required were mixed together and allowed to stand until the carbon monoxide elimination was completed. The product was filtered and the solvent permitted to evaporate. A good yield of violet amorphous product was observed.

The following table shows the anti-knock rating of some of the compounds of this invention as compared to the anti-knock rating of an unleaded gasoline of commercial premium grade specification using the ASTM research octane method.

TABLE 1

Additive at 5 g. per gal. concentration	ASTM research octane number
None	84.5
Propargyl alcohol dicobalt hexacarbonyl	91.0
Propargyl acetate dicobalt hexacarbonyl	89.6
Propargyl trichloroacrylate dicobalt hexacarbonyl	85.7
Propargyl p-nitrobenzoate dicobalt hexacarbonyl	85.7
Propargyl benzoate dicobalt hexacarbonyl	85.5

From the above table it can be seen that reaction products of acetylenic alcohols and their esters and cobalt carbonyl have definite value as anti-knock agents in motor fuel and the preferred products, propargyl alcohol dicobalt hexacarbonyl and propargyl acetate dicobalt hexacarbonyl, are particularly effective.

The following table demonstrates the effectiveness of the preferred additive propargyl alcohol dicobalt hexacarbonyl in various amounts up to its most effective concentration.

TABLE 2

Concentration of additive g. per gallon	ASTM research octane number
None	84.0
0.43	85
1.0	85.5
3.0	88.7
5.0	91.0

The foregoing table shows that the reaction products of this invention have utility in additive amounts of as little as 0.4 g. per gallon, or specifically 0.43 g. per gallon as shown. Further, it is seen that the value of the compounds increases as the concentration increases up to amounts of about 3 to 5 g. per gallon. We have found that there is little commercial value in the use of amounts over the preferred 5 g. per gallon. However, such amounts up to the limit of solubility of the reaction product in the fuel may be used.

Obviously, many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A liquid hydrocarbon fuel boiling within the gasoline range containing a reaction product of dicobalt octacarbonyl and an acetylenic compound, in an amount sufficient to lend anti-knock properties to the fuel, said reaction product having the following general formula:

$$R—O—R'\cdot Co_2(CO)_6$$

wherein R is selected from the group consisting of hydrogen, aliphatic acyl hydrocarbon, halogen substituted aliphatic acyl hydrocarbon, aroyl hydrocarbon, and nitro substituted aroyl hydrocarbon radicals, said hydrocarbon radicals having from 1 to 20 carbon atoms, and R' is a radical selected from the group consisting of aliphatic, hydroxy substituted aliphatic, and cyclo-aliphatic radicals containing from 3 to 20 carbon atoms.

2. A fuel as described in claim 1 wherein R' is an aliphatic radical containing three carbon atoms.

3. A fuel as described in claim 2 wherein R is hydrogen.

4. A fuel as described in claim 2 wherein R is an acetyl radical.

5. A fuel as described in claim 2 wherein R is a halogenated acetyl radical.

6. A fuel as described in claim 2 wherein R is a benzoyl radical.

7. A fuel as described in claim 2 wherein R is a nitro substituted benzoyl radical.

8. A liquid hydrocarbon fuel boiling within the gasoline range containing about 3 to 5 grams per gallon of the reaction product of dicobalt octacarbonyl and propargyl alcohol, said reaction product having the following formula:

$$R—O—R'\cdot Co_2(CO)_6$$

wherein R is hydrogen and R' is an aliphatic radical containing three carbon atoms.

9. A liquid hydrocarbon fuel boiling within the gasoline range containing about 3 to 5 grams per gallon of the

reaction product of dicobalt octacarbonyl and propargyl acetate, said reaction product having the following formula:

$$R—O—R'\cdot Co_2(CO)_6$$

wherein R is an aliphatic acyl hydrocarbon radical containing two carbon atoms and R' is an aliphatic radical containing three carbon atoms.

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