United States Patent Office 3,037,038 Patented May 29, 1962

3,037,038
MANGANESE CARBONYL POLYTERTIARY PHOSPHINE COMPOUNDS

James D. Johnston, Gene E. Schroll, and Hymin Shapiro, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed July 30, 1958, Ser. No. 751,836
8 Claims. (Cl. 260—429)

This invention relates to novel manganese compounds and more particularly to manganese carbonyl compounds which are particularly useful as additives to fuel, especially antiknocks.

Manganese carbonyl compounds have been known for many years [Hurd et al., J.A.C.S., 71, 1819 (1949)]. More recently U.S. Patent No. 2,822,247, Hnizda, disclosed a process for producing manganese pentacarbonyl dimer and more fully characterized this compound. It is a yellow crystalline solid melting at 156.5° C.

Manganese pentacarbonyl dimer is a powerful antiknock. It is materially better than iron carbonyl, for example, because it does not cause excessive wear in internal combustion engines. Moreover, while it is sufficiently volatile and inductible for use as a fuel additive, it is materially not too volatile from a toxicity standpoint and, therefore, has great advantage for commercial application as an antiknock. Best results are obtained when it is used in conjunction with other antiknocks, such as tetraethyllead, with which it is synergistic. In such mixtures, the manganese carbonyl is employed in a concentration of about 0.1 to 2.0 grams of manganese per gallon of gasoline containing about 3 cc. of tetraethyllead. However, commercial use of this mixed antiknock virtually requires the concurrent use of large quantities of phosphorus or other similar compounds to correct or prevent malfunctions in the engine, resulting from deposition of manganese or lead-containing combustion products. Specifically, exhaust valve life and spark plug life are materially reduced in the absence of such corrective agents. Thus, it is normal to employ in the fuel from about two to four theories of phosphorus based on manganese, i.e., two to four mole equivalents of phosphorus based upon the formation of $Mn_3(PO_4)_2$ or about 0.1 to 0.5 based upon the formation of $Pb_3(PO_4)_2$. Since manganese metal is the only active component in the added components to the leaded gasoline, most of the weight and expense of the added components is expended in organo groups in the molecule which merely solubilize the manganese or correct adverse affects of the manganese and lead combustion products. Thus, when tricresylphosphate (a known corrective agent) is employed in a four-theory mixture with manganese pentacarbonyl, the active component (manganese) is only about 2 percent of the total mixture added to the leaded gasoline. Therefore, the beneficial economics attributable to the manganese pentacarbonyl is considerably reduced by the cost of inert or extraneous organic groups in the manganese and phosphorus compounds.

It is accordingly an object of this invention to provide novel fuel soluble manganese compounds and especially compounds suitable for use as fuel additives. Another object is to provide novel phosphorus-containing manganese compounds which are relatively stable to heat and water, particularly when dissolved in hydrocarbons, such as gasoline and other fuels. Still another object is to provide such compounds which are useful in leaded gasoline, which compounds have at least two theories of phosphorus directly bonded to the manganese atom. Another object is to provide compounds of the above type in which the manganese metal is a relatively large fraction of the total weight of the manganese and phosphorus compound. Other objects and advantages of this invention will be more apparent in the following description and appended claims.

These and other objects of the invention are accomplished by the provision of new and novel manganese carbonyl polytertiaryphosphite compounds. These compounds have from two to four phosphorus atoms directly bonded to the manganese metal and from three to one carbonyl groups, depending upon the number of phosphite groups, also bonded directly to the manganese metal. Thus, the present invention comprises manganese carbonyl tetraphosphites, manganese dicarbonyl triphosphites, manganese tricarbonyl diphosphites and the corresponding thiophosphites.

The compounds of this invention have surprising stability and solubility in organic solvents. They are also exceptional antiknocks which, in use, can be blended directly in fuels, such as gasoline. In view of the flexibility in the choice of the number and type of phosphite radicals, the molecule can be "tailor made" to provide the optimum volatility, solubility and other auxiliary properties to best suit the particular fuel or gasoline with which it is to be used. Moreover, the combination of the phosphorus atom in the same molecule with the manganese atom results in more efficient utilization and other beneficial results.

Of primary importance, the compounds of this invention have "built in" phosphorus corrective agents which serve the dual function of also providing solubility and stability to the manganese atom. Thus, the unnecessary or "inert" components of an antiknock mixture can be material decreased when using as antiknocks the compounds of this invention. Using the same example as above, for instance, where four theories of phosphorus are desired per atom of manganese, the resultant antiknock mixture can consist of as great as about 17 percent manganese, compared with only about 2 percent when using manganese pentacarbonyl. Thus, using the present invention, for each part of manganese metal, over eight parts of waste or extraneous material are eliminated, materially reducing the cost per unit antiknock increase.

The compounds of this invention as pointed out above can be mono-, di- or tricarbonyls containing from four to two molecules of phosphites or thiophosphites, respectively.

These phosphites can contain alkyl or aryl groups, or both. Typical examples of alkyl phosphites are manganese carbonyl tetrakis(trimethylphosphite), -(triethylphosphite), -(triisobutylphosphite), and -(trihexylphosphite). Aryl phosphites of this invention are manganese carbonyl tetrakis(triphenylphosphite), -(tritolylphosphite), -(tribiphenylphosphite), -(trinaphthylphosphite), etc. Suitable examples of mixed alkyl-aryl phosphites are manganese carbonyl (triphenylphosphite) tris(trimethylphosphite), manganese carbonyl tetrakis(phenyldimethylphosphite), manganese carbonyl (triphenylphosphite) tris-(tribenzylphosphite) and the like.

The monocarbonyl tetra-phosphorus derivatives can also contain thiophosphite groups. For example, very desirable compounds of this invention include the alkyl thiophosphites such as manganese carbonyl tetrakis(trimethylthiophosphite), -(triethylthiophosphite), -(triheptylthiophosphite) and the like. Arylthiophosphites are also suitable and include manganese carbonyl tetrakis-(triphenylthiophosphite), manganese carbonyl tetrakis-(tritolylphosphite) and the like. Mixed alkyl and aryl thiophosphites are also suitable such as manganese carbonyl bis(trimethylthiophosphite) bis(triphenylthiophosphite), manganese carbonyl (trimethylthiophosphite) tris-(triphenylthiophosphite).

The manganese dicarbonyl tris(triorganophosphites) of this invention likewise can contain simple phosphite and thiophosphite groups as well as mixtures of these groups.

Thus, typical examples of manganese dicarbonyl tris(triorganophosphites), in accordance with this invention, are manganese dicarbonyl tris(trimethylphosphite), -(trioctylphosphite), manganese dicarbonyl (trimethylphosphite) bis(triethylphosphite), etc. Compounds containing aryl groups are also suitable and include manganese dicarbonyl tris(triphenylphosphite), -(tritolylphosphite), -(trinaphthylphosphite) and mixed arylalkyl phosphites such as manganese dicarbonyl (trimethylphosphite) bis(triphenylphosphite).

Typical examples of tris(triophosphites) in accordance with this invention are manganese dicarbonyl tris(trimethylthiophosphite), -(triisobutylthiophosphite) and the like. Aryl derivatives are also suitable such as manganese dicarbonyl tris(triphenylthiophosphite), manganese dicarbonyl (trimethylthiophosphite) bis(tritolylthiophosphite) and manganese dicarbonyl (trimethylthiophosphite) bis(trixylylthiophosphite).

Typical examples of manganese tricarbonyl bis(triorganophosphite) compounds are manganese tricarbonyl, -bis(trimethylphosphite), -bis(triethylphosphite), -bis(triphenylphosphite), -(trimethylphosphite)(triphenylphosphite), -bis(trimethylthiophosphite), -bis(triphenylthiophosphite), -trimethylphosphite)(trimethylthiophosphite).

In general, the organo groups of the above manganese carbonyl phosphite compounds can contain from one to fifteen carbon atoms. When the compounds are employed as gasoline additives, it is preferred to employ organo groups having from one to six carbon atoms, and best results are obtained when a total of not more than ten carbon atoms are present on each phosphorus atom. In general, the compounds containing alkyl groups are preferred.

The above compounds can exist as either monomers or dimers depending greatly upon the temperature. In general, at higher temperatures the compounds tend to exist as monomers.

The compounds of this invention can be made by a number of different processes including the reaction of a manganese compound, such as a salt, with carbon monoxide and the desired phosphorus containing ligand. This reaction is carried out preferably in the presence of a reducing agent to obtain simultaneous reduction of the manganese to a zero valence state and the addition of the electron donating phosphorus groups to the so-reduced manganese metal. A more preferred process involves the reaction of a manganese carbonyl, e.g., manganese pentacarbonyl dimer, with the desired phosphorus containing ligand. Thus, manganese pentacarbonyl can be reacted with a tertiary phosphite and/or thiophosphite to displace two to four of the carbonyl groups.

Frequently the above processes are facilitated by the use of catalysts, particularly ultraviolet light. The latter increases the reaction rate and also, in general, facilitates the replacement of the third and fourth carbonyl groups from the manganese atom.

The above processes can be conducted at temperatures of about from 0° C. or below up to a temperature wherein the products or reactants decompose at a substantial rate, usually about 350° C. A more preferred operating temperature is from about 50° C. to 250° C. Pressures can be used and are frequently desirable, particularly when employing normally gaseous reactants. In general, pressures from subatmospheric to about 30,000 p.s.i. are suitable, and usually those from 0 to 1,000 p.s.i. give best results. The above reactions can be conducted either with or without a solvent or inert medium. Typical examples of solvents are hydrocarbons, halogenated hydrocarbons, ethers, esters, alcohols, amines, dimethyl formamide, and the like. Suitable hydrocarbons are hexane, heptane, n-decane, benzene, toluene, xylene, naphthalene, biphenyl petroleum ether and other hydrocarbons having up to about 20 carbon atoms. Typical halogenated hydrocarbons are chloroalkanes, e.g., ethyl chloride and propyl chloride, bromobutanes, fluoroethylenes, trichlorobenzene and the like. Other examples of suitable solvents are ethers such as dimethyl ether, dibutyl ether, anisole, dioxane, tetrahydrofuran, ethylene glycol dialkyl ethers, e.g., diethylene glycol dimethyl ether, -diethyl ether, -dibutyl ether, -methyl ethyl ether, and other diethylene glycol ethers having alkyl groups containing from 1 to 15 carbon atoms. Additional examples of solvents are butyl amine, cyclohexyl amine, dicyclohexyl amine, aniline, ethyl acetate, butyl propionate, methanol, ethanol, butanol, phenol, ethylene glycol, glycerine and the like.

The concentration of reactants is generally about stoichiometric quantities although excesses of one or more of the reactants can be employed. The solvent concentration can be from about stoichiometric equivalents, particularly when complexes are formed, to several mole equivalents, i.e., up to about 10 mole equivalents.

EXAMPLE I

A solution of 8 parts of manganese pentacarbonyl, 19 parts of triphenyl phosphite, and 150 parts of nonane was heated under reflux for 8 hours. Upon cooling, a heavy oil layer separated from the mixture. The heavy oil was recovered and dissolved in a hot benzene-hexane solution. Upon cooling, white crystals of manganese tricarbonyl bistriphenyl phosphite were obtained, melting point 137 to 139° C. Analysis of the product was C—61.89%; H—3.97%; Mn—7.12%, corresponding to the theoretical analysis of C—61.8%; H—3.98%; Mn—7.24%. The product is soluble in hydrocarbons, and especially in aromatics.

EXAMPLE II

A reaction vessel was charged with 10 parts of manganese pentacarbonyl dimer, 13 parts of tri-n-butyl phosphite, and 300 parts xylene. The solution was heated at 120° C. for 5 hours and then cooled. The mixture was filtered to remove a small quantity of black solids. The filtrate was concentrated under reduced pressure to give a yellow oil which analyzes as a mixture of manganese dicarbonyl tris(tributyl phosphite) and manganese tricarbonyl bis(tributyl phosphite).

EXAMPLE III

Example I is repeated except that triethylthiophosphite is employed in diethylene glycol dimethyl ether solvent at 80° C. to produce a mixture of manganese carbonyl tetrakis(triethylthiophosphite), manganese dicarbonyl tris(triethylthiophosphite), and manganese tricarbonyl bis(triethylthiophosphite).

When the above examples are repeated with triisopropyl, trixylylphosphite, trimethylthiophosphite, and triphenylthiophosphite, similar results are obtained.

The novel compounds of this invention can be employed, as pointed out above, with hydrocarbon fuels of the gasoline boiling range and lubricating oils for improving operating characteristics of spark ignition internal combustion engines. The compounds can be used in the fuels and lubricating oils by themselves or together with other additive components, such as scavengers, deposit modifying agents containing phosphorus and/or boron, and also other antiknock agents, such as tetraethyllead, etc. However, such additional corrective agents are not normally necessary nor desirable since the compounds of this invention contain the requisite correction agents as part of the molecule. Of even more importance, the corrective components, i.e., phosphorus compounds are intimately associated with the manganese atom, being in the same molecule, and more efficiently correct or modify the manganese upon decomposition in the engine cylinders. Thus, the antiknock compounds of this invention contain phosphorus which provides fuel solubility to the manganese and, upon decomposition, also modifies the manganese decomposition products to form volatile, non-corrosive, non-abrasive products which are readily and efficiently purged from the engine.

The compounds of this invention can be added directly to the hydrocarbon fuels or lubricating oils and the mixture subjected to stirring, mixing, or other means of agita-

tion until a homogeneous fluid results. Alternatively, the compounds of this invention may be first made up into concentrated fluids containing solvents, such as kerosene, toluene, hexane, and the like, as well as other additives such as additional scavengers, anti-oxidants and other antiknock agents, e.g., tetraethyllead. Still other components that can be present are discussed more fully hereinbelow. The concentrated fluids can then be added to the fuels.

In certain of the compositions of this invention, organolead compounds are used. Preferably, hydrocarbon lead compounds are employed, such as tetraphenyllead, tetratolyllead, and particularly tetraalkyllead compounds such as tetraethyllead, tetrapropyllead and the like. In general, the amount of organolead antiknock agent is selected so that its content in the finished gasoline is equivalent to at least about one gram of lead per gallon. In other compositions of this invention, cyclopentadienyl manganese tricarbonyl compounds are employed, with or without the lead compounds, usually in a concentration of at least 0.1 gram per gallon.

The quantities employed of compounds of this invention can be expressed as theories. A theory of phosphorus is the amount of phosphorus required to convert the lead present to lead orthophosphate, $Pb_3(PO_4)_2$, that is, a theory of phosphorus based on lead represents an atom ratio of two atoms of phosphorus to three atoms of lead. When based on manganese, a theory of phosphorus likewise represents two atoms of phosphorus for every three atoms of manganese, to form manganese phosphate, $Mn_3(PO_4)_2$. The manganese compounds of this invention are preferably used in amount sufficient to provide excess theories of phosphorus, i.e., to provide phosphorus to react with the added lead compounds or other metal antiknocks.

To illustrate the variety of ways in which fuel mixtures can be formulated to provide the antiknock improvement and to simultaneously incorporate adequate corrective agents in the fuel composition, a commercial fuel having an initial boiling point of 90° F. and a final boiling point of 406° F. is blended with 3 cc. of tetraethyllead per gallon. To this mixture is then added various manganese carbonyl phosphite compounds in accordance with this invention, as well as other scavengers when desired. The following table shows a variety of combinations which can be employed to provide very effective fuel mixtures for use in internal combustion engines.

Table

Mn Compound	Mn, Grams/Gal.	Theories		
		P	Cl [1]	Br [2]
$Mn(CO)_3[P(OCH_3)_3]_2$	0.112	0.4	0.5	0.5
$Mn(CO)_3[P(OC_2H_5)_3]_2$	0.28	1.0	1.0	0.5
$Mn(CO)[P(OCH_3)_3]_4$	0.35	1.25		1.5

[1] Cl as ethylene dichloride.
[2] Br as ethylene dibromide.

When employing the compounds of this invention together with halogen scavengers, various halogen-containing organic compounds having from 2 to about 20 carbon atoms can be used in such relative proportions that the atom ratio of manganese to halogen is from about 50:1 to about 1:12. The scavenger compounds can be halohydrocarbons both aliphatic and aromatic in nature, or a combination of the two, with halogens being attached to carbons either in the aliphatic or the aromatic portions of the molecule. The scavenger compounds may also be carbon, hydrogen, and oxygen-containing compounds, such as haloalkyl ethers, halohydrins, haloesters, halonitro compounds, and the like. Still other examples of scavengers that may be used in conjunction with the manganese compounds of this invention, either with or without hydrocarbolead compounds, are illustrated in U.S. Patents 2,398,281 and 2,479,900–903, and the like. Mixtures of different scavengers may also be used. These fluids can contain other components as stated hereinabove. In like manner, manganese-containing fluids are prepared containing from 0.01 to 1.5 theories of phosphorus for the added lead antiknock in the form of phosphorus compounds, other than the phosphites of this invention, when necessary. To make up the finished fuels, the concentrated fluids are added to the hydrocarbon fuel in the desired amounts and a homogeneous fuel is obtained by mixing, agitation, etc.

The ratio of the weight of manganese to lead in fluids and fuels containing these components can vary from about 1:100 to about 50:1. A preferred range of ratios, however, when both the manganese compounds of this invention and hydrocarbolead compounds are employed, is from about 1:70 to about 30:1. For example, the addition of 0.04 gram of manganese per gallon in the form of manganese dicarbonyl tris(trimethylphosphite) to a commercial fuel having an initial boiling point of 90° F. and a final boiling point of 406° F. and containing 3.17 grams of lead per gallon in the form of tetraethyllead improves the antiknock qualities of the fuel by up to 1–10 octane numbers, depending upon the particular fuel employed. The ratio of manganese to lead on a weight basis is 1:79.3 in this case. In like manner, the addition of six grams of manganese per gallon to the same fuel containing 0.2 gram of lead per gallon in the form of tetraethyllead results in an even greater improvement in the antiknock quality of the fuel. The manganese-to-lead ratio in this case is 30:1.

The following examples are illustrative of fluids and fuels containing the new compounds of the present invention.

EXAMPLE IV

A concentrated fluid is prepared containing kerosene, a blue dye, and 10 parts of manganese as manganese tricarbonyl bis(tritolylphosphite) for every 0.02 part of lead in the form of diethyldimethyllead. This fluid is then blended with a commercial hydrocarbon fuel having an initial boiling point of 90° F. and a final boiling point of 394° F. in an amount sufficient to provide ten grams of manganese and 0.02 gram of lead per gallon.

EXAMPLE V

A fluid is prepared containing 100 parts of manganese tricarbonyl bis(triethylthiophosphite), 25 parts of manganese as cyclopentadienyl manganese tricarbonyl. This is blended with gasoline having an initial boiling point of 112° F. and a final boiling point of 318° F. in an amount such as to provide 1.0 gram of manganese as the phosphite, 0.25 gram of manganese as the tricarbonyl and 1.58 grams of lead per gallon.

EXAMPLE VI

To a fuel containing 0.1 gram of lead per gallon as diphenyldiethyllead, 1.0 theory of bromine as ethylene dibromide, and 0.2 theory of phosphorus in the form of tricresylphosphate, is added manganese carbonyl tetrakis(trimethylphosphite) in an amount equivalent to 0.03 gram of manganese per gallon. This small amount of manganese in the form of the compounds of this invention provides a considerable increase in the antiknock quality of the fuel as shown upon testing in a single-cylinder engine.

Other fuels and fluids are prepared in the same manner as illustrated hereinabove which contain other deposit-modifying agents, such as boric acid, borate esters, boronic esters, etc. Likewise, lubricating oils containing from about 0.1 to about 5 weight percent iron in the form of the manganese phosphite compounds of this invention are prepared, and these lubricating oils, when used in reciprocating engines, are found to have a beneficial effect on engine cleanliness and in the reduction of combustion chamber deposits.

As stated hereinabove, the amount of manganese that can be employed in the form of manganese phosphite com-

pounds of this invention in hydrocarbon fuels of the gasoline boiling range varies from about 0.015 to about 10 grams of manganese per gallon, preferably 0.03 to 6 grams of manganese per gallon. In addition, the fuel can also contain organolead antiknock compounds, such as tetraethyllead, in amounts equivalent to from about 0.02 to about 13.2 grams of lead per gallon.

The new antiknock agents of this invention may be mixed with antioxidants, such as alkylated phenols and amines, metal deactivators, phosphorus compounds, and other antiknock agents, such as amines and alkyllead compounds; anti-rust, and anti-icing agents, and wear inhibitors, may also be added to the antiknock composition or fuel containing the same.

In like manner, the fuels to which the antiknock compositions of this invention are added may have a wide variety of compositions. These fuels generally are petroleum hydrocarbon mixtures suitable for use in a spark ignition internal combustion engine. These fuels can contain all types of hydrocarbons, including paraffins, both straight and branched chain; olefins; cycloaliphatics containing paraffin or olefin side chains; and aromatics containing aliphatic side chains. The fuel type depends on the base stock from which it is obtained and on the method of refining. For example, it can be a straight run or processed hydrocarbon, including thermally cracked, catalytically cracked, reformed fractions, etc. When used for sparkfired engines, the boiling range of the fuel components can vary from zero to about 430° F., although the boiling range of the fuel blend is often found to be between an initial boiling point of from about 80° F. to 100° F. and a final boiling point of about 430° F. While the above is true for ordinary gasoline, the boiling range is a little more restricted in the case of aviation gasoline. Specifications for the latter often call for a boiling range of from about 82° F. to about 338° F., with certain fractions of the fuel boiling away at particular intermediate temperatures.

The hydrocarbon fuels in which the antiknock agent of this invention can be employed often contain minor quantities of various impurities. One such impurity is sulfur, which can be present either in a combined form as an organic or inorganic compound, or as the elemental sulfur. The amounts of such sulfur can vary in various fuels from about 0.003 percent to about 0.50 percent by weight. Fuels containing quantities of sulfur, both lesser and greater than the range of amounts referred to above, are also known. These fuels also often contain added chemicals in the nature of antioxidants, rust inhibitors, dyes and the like.

A particular advantage of the new compositions of matter of the present invention is the fact that by proper selection of the individual groups comprising such compositions, compounds having "tailor made" characteristics can be obtained. Thus, by the proper selection of the organo group, it is possible to prepare compounds possessing differing degrees of stability, volatility and solubility. Likewise, the selection of these constituents also enables the preparation of compounds of diverse applicability.

While the compounds of the present invention have been disclosed above for use as antiknocks in gasoline, the compounds of this invention are also useful as additives to hydrocarbons in general. Thus, in addition to fuels for internal combustion engines, these compounds are also useful to improve burner fuels, jet fuels, diesel fuels, turbine engine fuels, etc., to reduce smoke, and other undesirable by-products and to generally improve the burning characteristics of the hydrocarbons. Likewise, these compounds are useful as catalysts, as chemical intermediates in the manufacture of other valuable chemicals and the like.

We claim:

1. A manganese carbonyl polytertiary phosphite compound of the general formula

$$Mn[P(XR)_3]_n(CO)_{5-n}$$

wherein n is an integer from 2 to 4, X is selected from the group consisting of oxygen and sulfur, and R is a hydrocarbon group containing from one to fifteen carbon atoms, said hydrocarbon group being selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

2. The compound of claim 1 further defined wherein X is oxygen and R is an alkyl radical containing from one to six carbon atoms.

3. The compound of claim 1 further defined wherein X is oxygen and R is an aryl radical.

4. The compound of claim 1 further defined wherein X is sulfur and R is an alkyl radical containing from one to six carbon atoms.

5. The compound of claim 1 further defined wherein X is sulfur and R is an aryl radical.

6. Manganese tricarbonyl bis(triphenylphosphite).

7. Manganese dicarbonyl tris(tributylphosphite).

8. Manganese tricarbonyl bis(tributylphosphite).

References Cited in the file of this patent

UNITED STATES PATENTS

2,575,003	Caron et al.	Nov. 13, 1951
2,591,503	Bottoms	Apr. 1, 1952
2,818,416	Brown et al.	Dec. 31, 1957
2,818,417	Brown et al.	Dec. 31, 1957

OTHER REFERENCES

"Zeitschrift für Naturforschung" (Hieber et al.), vol. 12*b*, July 1957 (page 479 relied on).

"Science" (Irvine et al.), vol. 113, pp. 742 to 743 (1951), page 742 relied on.