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CYCLOPENTADIENYL MANGANESE TRICARBONYL-CONTAINING FUELS, LUBES AND ADDITIVE FLUIDS

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This invention relates to new compositions of matter and in particular to new fuel compositions which possess numerous benefits in connection with alleviation of modern day engine problems. This application is a continuation-in-part of our copending application, Serial No. 622,237, filed November 15, 1956, now abandoned.

The fuels and lubricants used in today's high compression automotive engines cause deposits to be formed during combustion. These deposits which are derived from the fuels and lubricating oils and the additives therein collect on essentially all parts of the combustion chamber including the valves, the spark plugs and the cylinder walls. The formation of these deposits leads to several problems.

When a new engine is operated before combustion chamber deposits have had a chance to build up, the engine is found to have a certain octane requirement. As it is operated, the octane requirement gradually increases as deposits are built up. After a certain operating time the deposits reach a state of equilibrium in which the rate of their build-up is equalled by the rate of their removal by one means or another. When this happens, the octane requirement of the engine has become stabilized and levels off at essentially a constant value. This equilibrium requirement of the engine is frequently as much as 12 to 15 octane numbers above that of the clean engine before deposit formation. This necessitates the use of gasoline of unnecessarily high octane number for knock-free performance of the car.

When compounds formed by the burning of fuel, lubricating oil and their additives are deposited on the insulator of the spark plugs, these deposits provide an alternate path from the center electrode to the ground electrode. If the resistance of deposits which form this path is sufficiently low the loss of electrical energy through the deposit may prevent the voltage from rising to that required to fire the plug. Such a fouled plug will normally misfire throughout the speed range of the engine resulting in poor acceleration, engine roughness, reduced top speed of the vehicle and high consumption of the fuel.

Deposit-induced ignition (surface ignition) results when glowing combustion chamber deposits ignite the fuel charge at a time other than when it would be ignited by the spark plug. Such ignition may result in wild erratic knock or engine roughness which is objectionable to the motorist. When the antiknock quality of a fuel has to be increased to suppress such combustion this represents a waste of octane numbers. Surface ignition also prevents the engine designer from making optimum use of antiknock quality in combustion chambers requiring close combustion control.

It is an object of this invention to provide new compositions of matter. A more specific object is to provide new fuel compositions. Among the other objects of

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this invention are the alleviation of engine problems including octane requirement increase, spark plug fouling and surface ignition. Still further objects will be apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing new compositions of matter which comprise gasoline containing cyclomatic compounds having the general formula



wherein M is a metal, namely, manganese; A is a cyclomatic radical, that is, a cyclopentadienyl radical and B is an electron donating group such that $a_n + 5x + py = S$, wherein S is the atomic number of an inert gas of the fourth period; namely, krypton; x is a small whole integer, namely, 1; y is a small whole integer, namely, 3; n is a period of the periodic table, namely, the fourth period; p is the number of electrons donated by the electron donating group, namely, 2, and a is the atomic number of the metal, namely, 25. The amount of such compounds present in our gasoline compositions is usually regulated such that it is equivalent to 0.1 to 6.0 grams of manganese per gallon. Although the deposit modifying effects are accomplished with any amount of additive within this range certain important auxiliary benefits are accrued when using amounts in the upper portion of the range.

In other words, the new compositions of this invention comprise gasoline containing from about 0.1 gram per gallon to 6.0 grams per gallon of manganese as a cyclopentadienyl manganese tricarbonyl wherein the cyclopentadienyl radical contains 5 to 13 carbon atoms. As will be seen below such compositions give rise to a great reduction in octane requirement increase (ORI) and surface ignition of the automotive engine. Outstanding benefits are obtained with regard to these factors and also with regard to wear throughout the aforesaid concentration range. Many important benefits are realized at even lower manganese concentrations such as 0.05 or 0.005 gram of manganese per gallon. Concentrations as high as 10 grams of manganese per gallon are also effective.

The compositions of this invention can also contain organolead antiknock agents, particularly alkyllead compounds with the concomitant scavengers. Generally the amount of such organolead material will be such to give a lead content of from about 1 to about 8 grams per gallon. Lead contents as low as 0.02 and as high as 13.2 grams per gallon can also be used.

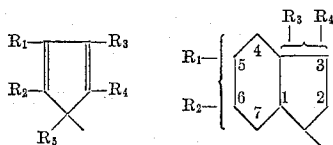
For best results for increasing spark plug life the above compositions should contain additionally at least 0.015 weight percent of sulfur and preferably between 0.015 and 0.065 weight percent of this element. However, benefits are obtained with sulfur concentrations between 0.003 and 0.3 weight percent. Spark plug life with such compositions is spectacularly increased. These compositions may also contain organolead antiknock agents in the amounts specified above.

Reference to the generic formula described hereinabove indicates that there are three primary constituents of the new compositions of matter of the present invention. They are the metallic constituent manganese designated as M, the cyclomatic or cyclopentadienyl radical

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designated as A and an electron donating group, namely, carbon monoxide, designated as B.

The constituent designated by the symbol A in the formula presented hereinbefore comprises a cyclomatic radical, that is, a cyclopentadiene-type hydrocarbon radical which is a radical containing the cyclopentadienyl moiety. In general such cyclomatic hydrocarbon groups can be represented by the formulae



where the R's are selected from the group consisting of hydrogen and univalent organic hydrocarbon radicals.

A preferred class of cyclomatic radicals suitable in the practice of this invention are those which contain from 5 to about 13 carbon atoms. These are exemplified by cyclopentadienyl, indenyl, methylcyclopentadienyl, propylcyclopentadienyl, diethylcyclopentadienyl, phenylcyclopentadienyl, tert-butylcyclopentadienyl, p-ethylphenylcyclopentadienyl, 4-tert-butyl indenyl and the like. The compounds from which these are derived are preferred as they are more readily available cyclomatic compounds and the metallic cyclomatic coordination compounds obtainable from them have the more desirable characteristics of volatility and solubility which are prerequisites of superior hydrocarbon additives. Moreover, they give the most outstanding results.

The third primary constituent of the new compositions of matter of the present invention is designated as an electron donating group, namely, carbon monoxide.

Thus, representative compounds of the present invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, methyl indenyl manganese tricarbonyl, fluorenyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, methylpropylcyclopentadienyl manganese tricarbonyl, phenylcyclopentadienyl manganese tricarbonyl and the like.

Still another preferred class of compounds falling within the scope of the instant invention are compounds having the formula MA_xB_y , as defined above, which are liquids at ordinary temperatures. When compounds of the above formula, which are liquids, are employed as additives, they have the important advantages of being readily handled and easily blended with liquid hydrocarbons. Further, when employed in liquid hydrocarbon fuel as deposit modifying additives, these compounds are more readily inductible into the cylinders of a multi-cylinder internal combustion engine. An outstanding example of this class of compound is methylcyclopentadienyl manganese tricarbonyl.

The additives of this invention may be conveniently prepared by reaction of the corresponding bis(cyclopentadienyl)manganese compound with carbon monoxide under pressure. The identity of the cyclopentadienyl radicals in this intermediate corresponds to those desired in the final product. The bis(cyclopentadienyl)manganese intermediates can, in turn, be conveniently prepared by reaction of a cyclopentadienyl alkali metal compound such as cyclopentadienyl sodium with a manganese salt such as manganous chloride. This method of preparation is illustrated in the following examples.

EXAMPLE I

A reaction vessel equipped with means for charging and discharging liquids and solids, gas inlet and outlet means, temperature measuring devices, heating and cooling means, means for agitation, and means for condensing vapors, was flushed with pre-purified nitrogen. To

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the flask were then added 400 parts of tetrahydrofuran and 23 parts of sodium dispersed in 23 parts of mineral oil. An atmosphere of nitrogen was maintained in the reaction vessel throughout the run. The vessel was cooled to 10° C. and 66.7 parts of freshly-distilled cyclopentadiene was added in small increments with agitation while maintaining the temperature below 15° C. After the addition of the cyclopentadiene, the temperature was allowed to rise to 23° C. over a period of about two hours when the completion of the formation of the sodium cyclopentadiene was evidenced by the cessation of hydrogen evolution. To this solution of cyclopentadienyl sodium in tetrahydrofuran was added 63 parts of anhydrous manganous chloride. The mixture was heated and maintained at reflux temperature for 20 hours. At the end of this time, the solvent was removed by distillation under reduced pressure and the product purified by sublimation at a pressure of about 2 millimeters of mercury at about 130° C., producing 48.64 parts, 52.5 percent yield, of lustrous, brown-black bis(cyclopentadienyl)manganese crystals. Analysis of the product showed it to contain 65.9 percent carbon and 5.44 percent hydrogen, corresponding to the formula $(C_5H_5)_2Mn$, calculated 64.9 percent carbon and 5.41 percent hydrogen. The bis(cyclopentadienyl)manganese oxidized readily in air and should, therefore, be kept in an inert atmosphere, such as nitrogen.

The bis(cyclopentadienyl)manganese together with 88 parts of diethylether was charged under a nitrogen atmosphere to a pressure resistant vessel which had been flushed with prepurified nitrogen. The vessel was equipped with gas inlet and outlet valves, temperature and pressure measuring devices, heating and cooling means, and means for agitation. The vessel was pressured with carbon monoxide to 1975 p.s.i. at 26° C. and then the temperature was slowly raised to 158° C. The reaction between the CO and $(C_5H_5)_2Mn$ was conducted at a temperature within the range of 22° C.-158° C. and at a pressure ranging from 1160 to 2800 p.s.i. for a period of 7 hours. The excess CO was then released below 30° C. and the reaction mixture, a yellow-brown slurry, was removed from the vessel. The solids were removed by filtration and the residue washed with ether to remove the last traces of product which is soluble in the ether. The ether was then distilled off at reduced pressure and the product, cyclopentadienyl manganese tricarbonyl, purified by sublimation. It consisted of a yellow air-stable, water-insoluble solid having a melting point of 77° C. It is readily soluble in most hydrocarbons and organic solvents including benzene, hydrocarbon fuels, lube oils, hexane, ether, alcohol, acetone, etc. Analysis showed it to contain 47.2 percent C, 2.48 percent H, and 26.9 percent Mn, corresponding to the formula



calculated 47.0 percent C, 2.47 percent H, and 26.9 percent Mn. The yield was 75.4 percent based on the amount of dicyclopentadienyl manganese intermediate obtained, or 39.2 percent based on the amount of $MnCl_2$ employed.

EXAMPLE II

The procedure of Example I was followed employing 400 parts of tetrahydrofuran, 23 parts of sodium dispersed in 23 parts of mineral oil, 80 parts of freshly-distilled methylcyclopentadiene, and 63 parts of powdered $MnCl_2$, containing 3.11 percent water. The manganous chloride was added to the methylcyclopentadienyl sodium solution at a temperature of 20° C. After maintaining the mixture at reflux temperature for two hours, the intermediate bis(methylcyclopentadienyl)manganese was separated by distillation at reduced pressure under nitrogen. It was a viscous, reddish-brown liquid which crystallized on standing. Analysis showed it to contain 66.7 percent carbon and 6.54 percent hydrogen, corresponding to the formula $(C_5H_7)_2Mn$; calculated 67.6

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percent C and 6.62 percent H. The yield was 84.3 percent based on the amount of $MnCl_2$ employed. The bis(methylcyclopentadienyl)manganese is spontaneously combustible and, therefore, should not be exposed to oxygen of the atmosphere.

The intermediate was transferred under nitrogen to the pressure resistant vessel and the vessel charged with CO and heated from about 22° C.-148° C. at 680 to 2175 p.s.i.g. The reaction was essentially completed in about 1 hour as indicated by the cessation of CO uptake. The vessel was then cooled, the product mixture removed, and the resultant product, methylcyclopentadienyl manganese tricarbonyl, purified by fractional distillation at reduced pressures. The product distilled at 106.5° C. at a pressure of 12 millimeters of mercury, and was a yellow-orange liquid having a freezing point of -0.75° C., a refractive index (n_D^{20}) of 1.5873, and a density (d_{20}^4) of 1.3942. It has a vapor pressure ranging from 8 millimeters at 100° C. to 360.6 millimeters at 200° C. It is readily soluble in hydrocarbons and most organic solvents, including hexane, hydrocarbon fuels, such as gasoline and diesel fuels, lubricating oils, alcohols, ether, acetone, ethylene glycol, etc. Analysis of the compound showed 24.7 percent manganese, 49.9 percent carbon, and 3.16 percent hydrogen; calculated 25.2 percent Mn, 49.6 percent C, and 3.21 percent H. The yield was 77.8 percent based on the amount of $MnCl_2$ employed.

In the above method of preparation, good results are also obtained in the manufacture of other compounds of this invention such as indenyl manganese tricarbonyl, ethyl manganese tricarbonyl, dimethyl manganese tricarbonyl and the like.

When compounds of the type described above are blended with gasoline in amounts corresponding to the manganese concentrations sets forth hereinabove, spectacular results are obtained in the alleviation of ORI and surface ignition. These deposit modifying effects are obtained both in the presence and absence of organolead antiknock agents. Drastic increases in spark plug life are also imparted by our compositions, particularly when the gasoline also contains sulfur in the stated amounts. The sulfur can be either naturally-occurring sulfur or added sulfur in the form of gasoline-soluble organic compounds. In either case this sulfur is typically in the form of elemental sulfur, hydrogen sulfide, mercaptans, sulfides, thiophenes, disulfides, polysulfides and the like. The benefits of the invention are realized in either event.

The following examples illustrate the deposit-modifying compositions of this invention. The types of gasolines used are characterized as follows:

Gasoline	Paraffins, Percent	Olefins, Percent	Aromatics, Percent	Naphthenes, Percent	End Point, °F.	Gravity, °API	Vapor Pressure, p.s.i.
A-----	45.2	29.4	25.4	-----	390	59.0	8.9
B-----	70.1	15.6	14.3	-----	385	64.4	-----
C-----	39.1	21.1	17.1	22.8	426	61.4	11.7
D-----	35.3	34.2	30.5	-----	378	56.2	8.1
E-----	44.0	17.9	38.1	-----	366	54.6	7.8

EXAMPLE III

To 1000 gallons of gasoline A is added cyclopentadienyl manganese tricarbonyl in amount such that the concentration of manganese is 0.1 gram per gallon.

EXAMPLE IV

To 1000 gallons of gasoline B is added methylcyclopentadienyl manganese tricarbonyl in amount such that the concentration of manganese is 1.0 gram per gallon.

EXAMPLE V

To 1000 gallons of gasoline C containing 3 millimeters of tetraethyllead as 62-Mix (1 theory of ethylene dichloride and 0.5 theory of ethylene dibromide; 1 theory being that amount of scavenger which provides 2 atoms

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of halogen for each atom of lead present in the organolead compound), is added indenyl manganese tricarbonyl in amount equal to 0.25 gram of manganese per gallon. To two more batches of this same leaded fuel is added indenyl manganese tricarbonyl to a manganese concentration of 0.1 gram per gallon and of 6.0 grams per gallon respectively.

EXAMPLE VI

To 1000 gallons of gasoline D containing 0.03 weight percent sulfur is added butylcyclopentadienyl manganese tricarbonyl in amount corresponding to 0.1 gram of manganese per gallon.

EXAMPLE VII

To 1000 gallons of gasoline E containing 0.65 weight percent sulfur is added methylcyclopentadienyl manganese tricarbonyl in amount corresponding to 4.0 grams of manganese per gallon.

EXAMPLE VIII

To 1000 gallons of gasoline A containing 0.03 weight percent sulfur and 3 milliliters of tetramethyllead per gallon with 1.0 theory of dibromobutane as scavenger is added dimethylcyclopentadienyl manganese tricarbonyl in amount corresponding to 2.4 grams of manganese per gallon.

EXAMPLE IX

To 1000 gallons of gasoline B containing 0.03 weight percent of sulfur and 8 grams per gallon of lead as tetraethyllead with 1.0 theory of ethylene dibromide as scavenger is added allylcyclopentadienyl manganese tricarbonyl in amount corresponding to 0.1 gram of manganese per gallon.

EXAMPLE X

To 1000 gallons of gasoline C containing 0.03 weight percent sulfur and 1 gram per gallon lead as tetraethyllead with 1.0 theory of ethylene dichloride and 0.5 theory of dibromotoluene as scavengers is added fluorenyl manganese tricarbonyl in amount corresponding to 3.0 grams of manganese per gallon.

To demonstrate the great benefit the present compositions give with respect to ORI and surface ignition the following dynamometer procedure was used.

This dynamometer test involves the use of a modern V-8 automotive engine run 24 hours per day on a cycling schedule to evaluate the effects of additives on octane requirement increase and surface ignition requirement. The cycle is intended to represent a light-duty suburban-type of driving condition. The dynamometer speed and load conditions of the cycle are as follows:

Duration, sec.	Type of Operation	Speed and Load
110-----	Road Load-----	1,500 r.p.m., 14 B.H.P.
15-----	Deceleration-----	1,500-700 r.p.m. ^a
20-----	Idle-----	700 r.p.m., no load.
15-----	Acceleration-----	700-1,500 r.p.m. ^b

^a Throttle against idle stop.

^b Throttle position set to give 7 in. Hg manifold vacuum at 1500 r.p.m.

This throttle position is constant throughout the acceleration then closes somewhat to give road-load power output at 1500 r.p.m.

Jacket coolant is maintained at 170 F., oil temperature at equilibrium, carburetor air 90-100 F., and ignition timing 5° retarded from standard setting.

The surface-ignition requirement is determined twice daily, using primary reference fuels. This rating is performed for 20 seconds at 1000 r.p.m., full throttle, with ignition timing 5° retarded from standard.

Knock requirements are obtained daily at 1000 r.p.m.,

full throttle, with ignition timing varied to obtain trace knock on each primary reference fuel blend. The standard spark advance setting is "bracketed" to obtain the octane number requirement of the engine. Surface ignition is distinguished from ordinary knock by cutting the ignition as soon as surface ignition is believed to be present during a rating. If surface ignition is present, the engine will continue to run and noise will be continued. Ordinary knock will not result in after-run or noise.

Each test starts with the engine clean in every respect, and continues until a relatively stable period of octane number requirement is reached.

In this procedure the initial stabilized octane requirement of the engine was 103 octane numbers when run on a fuel containing 3.0 milliliters of tetraethyllead per gallon as 62-Mix. When this same leaded fuel was run in the above procedure except that it contained additionally 0.25 gram per gallon of manganese as methylcyclopentadienyl manganese tricarbonyl the octane requirement was reduced to an octane number of 102. One-half gram of manganese as the same compound reduced the requirement to 101.

In these tests the surface ignition requirement of the engine when run on a fuel without manganese was 100. Addition of 0.25 gram of manganese to the fuel as methylcyclopentadienyl manganese tricarbonyl caused a reduction in this requirement to an octane number of 98.

In a similar test a stabilized octane requirement of 102.5 numbers was reduced to 101 octane numbers by the addition of 0.1 gram of manganese as methylcyclopentadienyl manganese tricarbonyl and to 99.2 octane numbers by addition of 0.25 gram of manganese as the same compound. Addition of 1.0 gram of manganese as this compound reduced the requirement to less than 99 octane numbers. In connection with this same procedure addition of gasoline containing 1.5 grams of manganese as methylcyclopentadienyl manganese tricarbonyl and containing no tetraethyllead reduced the equilibrium requirement from a 102 octane number to less than 99.

In the latter test the surface ignition requirement of the engine was 101 octane numbers. Addition of 0.125 gram of manganese as methylcyclopentadienyl manganese tricarbonyl reduced this requirement to 98.4 octane numbers and addition of 1.0 gram of manganese as this same compound reduced it to an octane number of 96.

In further tests an engine having a "clean" requirement of 98 was operated on gasoline containing 3 milliliters of lead as 62-Mix. After 90 hours of operation this engine had attained an equilibrium requirement of 102 octane numbers. After a total of 190 hours of operation the engine was operated on the same gasoline which additionally contained 0.25 gram of manganese as methylcyclopentadienyl manganese tricarbonyl. After a total operating time of 240 hours (50 hours on the manganese compound) the requirement had dropped down to 101 and after a total of 290 hours the requirement was 100. The composition of this invention thus halved the ORI.

In further tests an engine having a clean requirement of 96 was run on fuel containing 3 milliliters per gallon of tetraethyllead as 62-Mix and containing 0.01 percent sulfur. After 120 hours an equilibrium requirement of 102 had been attained. After 220 hours the engine was switched to the same fuel which additionally contained 1.0 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl. The requirement was immediately reduced and after 230 total hours was down to 101. At 300 hours the requirement had been lowered to 98, or by two-thirds. Thus, it is seen that the compositions of this invention provide significant reduction in ORI both in leaded and unleaded fuels. In general, results of this type are contained with fuels containing 0.1-6.0 grams of manganese as an additive of this invention.

To demonstrate the effect of the compositions of the instant invention on spark plug fouling the following procedure is used.

Lead fouling in passenger cars is most likely to result under the following conditions: (a) service consisting of long intervals of city or suburban driving followed by (b) infrequent and brief full-power demands as encountered in full throttle accelerations or passing on open highways. To reproduce these driving conditions on the dynamometer, tests are divided into two phases: a deposit forming schedule which meets the conditions of (a) above, and a spark plug rating which duplicates the (b) conditions. Test procedures are described briefly as follows.

DEPOSIT FORMING SCHEDULE

On the dynamometer the city driving schedule is reproduced by an automatically controlled cycle of loads and speeds as follows:

- (1) A 37 second repeating cycle consisting of a mild acceleration from 1000 r.p.m., no load, to 1600 r.p.m., road load.
- (2) Six second acceleration at approximately one-half throttle to 3100 r.p.m. (8 in. Hg at 3100 r.p.m.) repeated at three minute intervals.

Two cycling devices are used. Cycle 1 is produced by spring loading the throttle closing linkage against the surface of a cam that is motor driven through a set of reduction gears. Cycle 2 is controlled by an electric timer which actuates the throttle by the action of compressed air in a simple piston-cylinder device. Suitably located microswitches automatically control dynamometer loading. To break up any rigid pattern and to maintain the random nature of throttle variations, the two cycling devices are purposely out of synchronization.

Spark plug test sets are operated for 16 hour periods on the above schedule. Fuel-air ratio, ignition timing, and other factors that can affect plug performance are carefully controlled. At 16 hour intervals the plugs are removed from the engine for rating to determine their degree of fouling.

SPARK PLUG RATING

Spark plugs accumulate deposits in their respective dynamometer engines, but the ratings are always performed in one cylinder of an engine reserved for that purpose. Operating conditions in the cylinder are strictly controlled and instrumentation is provided to make a continuous record of spark plug deposit, shunt resistance and firing pattern. The spark plug rating is intended to reproduce a passenger car full throttle acceleration to approximately 80 m.p.h. For the 1956 V-8 engines used in our laboratory tests, rating is of 30 seconds duration and consists of a full throttle acceleration from 1500 r.p.m. road load to 3200 r.p.m. Approximately 3 seconds are required to reach 3200 r.p.m. and this speed at full throttle is held constant for the remaining 27 seconds. This duplicates the spark plug temperature-time relationship in a 1956 V-8 vehicle acceleration as determined by thermocouple spark plug temperature measurements. Schedules duplicating spark plug temperatures of other engine-transmission combinations have also been devised by means of the thermocouple plugs. Spark plugs are classified as failures if misfiring, accompanied by low deposit resistance, occurs during the first 15 seconds of rating. After rating the test plugs are returned for an additional 16 hours on the deposit buildup schedule. This cycle is repeated until three plug failures per set have been recorded, at which time the test is normally concluded. Test results are generally expressed in terms of average hours to three plug failures per set.

In such a procedure a gasoline containing 3 milliliters of tetraethyllead per gallon as 62-Mix was found to have an average spark plug life of 20 hours. When, however,

the same procedure was repeated on the same fuel except that it contained methylcyclopentadienyl manganese tricarbonyl, the spark life was increased to 60 hours at a manganese concentration of 0.25 gram per gallon. In a test with fuel containing 0.065 weight percent sulfur and 1.0 gram of manganese per gallon as a compound of this invention, the spark plug life was greater than 60 hours. Thus, the compositions of this invention are capable of increasing spark plug life at least 300 percent.

In another determination, a gasoline containing 3 milliliters of tetraethyllead per gallon but no cyclopentadienyl manganese tricarbonyl gave a spark plug life of 25 hours. When this fuel was treated with methylcyclopentadienyl manganese tricarbonyl at a concentration of 1.0 gram of manganese per gallon, no plug failures occurred in 160 hours. Thus, a composition of this invention improved plug life at least 640 percent. Still another gasoline containing 0.5 gram of manganese per gallon as a compound of this invention and 0.03 weight percent sulfur gave a spark plug life of 100 hours, a 400 percent improvement. Similar improvements are noted with gasoline containing 0.5 gram per gallon of manganese as a compound of this invention and 0.02 and 0.015 weight percent sulfur.

The deposit modifying properties of our compositions are also demonstrated by single-cylinder engine tests. To determine the effectiveness of our compositions in suppressing deposit-induced ignition (surface ignition), a commercially available premium gasoline base stock containing varying amounts of the compound is used as fuel in a single-cylinder CFR knock test engine equipped with an L-head cylinder. The oil employed in the test engine is a commercially available multigraded oil. All surface ignition data is corrected to 6.2 ml./hr. oil consumption. The test engine is equipped with an electronic device which automatically records surface ignition during the test period. Such apparatus includes an extra spark plug used as an ionization gap which is installed in a second opening in the combustion chamber. A mechanical breaker switch driven at camshaft speed is also provided which, when closed, makes the surface ignition counter ineffective for the duration of the normal flame in the combustion chamber. The breaker is open for 80 crankshaft degrees between 70° BTC (before top dead center) and 10° ATC (after top dead center). If a flame front induced early in the cycle by deposits reaches the ionization gap during this open period, the counter registers a surface ignition regardless of the audible manifestations. During normal combustion with ignition timing at TDC (top dead center) the flame front reaches the ionization gap at 15 to 18° during the period wherein the points are closed and no count is made. The actual test procedure consists essentially of operating the test engine on a cycling schedule alternating between the following conditions:

Duration, seconds.....	50	150
Speed, r.p.m.....	600 ± 30	900
Load.....	None.	Full
Fuel-Air ratio.....	.087 ± .004	.007 ± .001
Ignition timing.....	TDC	TDC
Coolant temperature, F.....	148 ± 3	148 ± 3
Oil temperature, F.....	160 ± 5	160 ± 5
Carburetor intake air, F.....	110 ± 5	110 ± 5

The effect of the composition on surface ignition is determined by comparing the number of surface ignitions per hour observed while using fuel containing our additive with the number observed when using the base stock. ORI is determined by comparing the requirement of the engine when run on standard fuel until equilibrium deposits are formed with the requirement when run with portions of the same fuel containing additives of this invention. Deposit weight is determined by direct measurement.

In these tests, compositions of this invention showed

substantial improvement with respect to all three problems—ORI, surface ignition and deposit weight. Our compositions are also useful in alleviating valve corrosion.

5 When other compounds of this invention such as indenyl manganese tricarbonyl, ethyl manganese tricarbonyl, dimethyl manganese tricarbonyl, and the like, are run through the same and similar tests substantially equivalent benefits in terms of ORI, surface ignition and spark plug fouling are obtained.

10 Another advantage which the additives of this invention possess is their extremely low wear characteristics. For example, it is found that an engine operated on a commercial hydrocarbon fuel of the gasoline boiling range containing 3.17 grams of lead per gallon in the form of tetraethyllead, 0.5 theory of bromine as ethylene dibromide, and 1.5 theory of chlorine as ethylene dichloride—the theories of halogen being based on the amount of lead present—and about 0.1 gram of manganese as methylcyclopentadienyl manganese tricarbonyl does not exhibit any increase in wear over the same fuel with no cyclo-
20 matic manganese tricarbonyl compounds present. The amount of wear was determined by the rate of loss in weight by the upper piston ring according to the method disclosed in U.S. 2,315,845. When, on the other hand, iron compounds such as iron carbonyl are employed together with tetraethyllead in fuels, the wear rate goes up considerably due to the presence of the iron.

30 It will be seen from the above that the amazing benefits of the present compositions are obtained when the amount of manganese is extremely low. A good range is from 0.1 gram of manganese per gallon to about 6.0 grams of manganese per gallon. However, as these data also show, the same good results are obtained when the manganese concentration is adjusted to be in the upper portion of this range. In many cases it is preferable to employ the high concentration since auxiliary benefits are obtained thereby. Ordinarily we prefer to use blends wherein the manganese content of the gasoline ranges up to about 6 grams per gallon as the cyclopentadienyl manganese tricarbonyl. This is true both in leaded and unleaded fuels. In such compositions, the antiknock value of fuels both leaded and unleaded is markedly increased. However, in the case of leaded fuels it is usually not necessary to go much above 3 grams of manganese per gallon. To illustrate, addition of 0.5 gram of manganese per gallon as cyclopentadienyl manganese tricarbonyl to an unleaded fuel having an octane number of 77.2 increased its octane rating to 86.3. The same additive at a concentration of 1.0 gram of manganese per gallon increased it to 89.4 and at 4.5 grams per gallon to 98.8. One-half gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl increased the octane number of the clear fuel to 86.3; one gram to 89.6 and 5 grams to 99.6.

45 Addition of 1.06 grams of lead per gallon as tetraethyllead to the same base fuel increased its octane number to 85.6. When cyclopentadienyl manganese tricarbonyl was added to this leaded fuel at a concentration of 1.0 gram per gallon, the octane number was raised to 91.7 and 3.0 grams of manganese per gallon as the same compound raised it to 98.9. Addition to this leaded fuel of 1.0 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl increased the octane rating to 92.1. Significant modification and valve corrosion effects are obtained at concentrations down to about 0.05 gram of manganese per gallon.

70 These and other compounds of the invention when used in higher and lower concentrations and with higher and lower organolead compound concentrations give similar antiknock improvement. Other auxiliary benefits, such as decrease in valve corrosion, are realized when our compositions containing from about 0.1 to 6.0 grams of

manganese per gallon as well as less than this amount are employed.

As the organolead antiknock which is a supplemental ingredient of certain of the compositions of this invention organolead compounds in general may be used. Preferable are hydrocarbon lead compounds such as tetraphenyllead, tetratolyllead and particularly tetraalkyllead compounds such as tetramethyllead, tetraethyllead, tetrapropyllead and the like. In general, the amount of organolead antiknock agent is selected so that its content of the gasoline is equivalent to about 1 to about 8 grams of lead per gallon of gasoline.

When tetraalkyllead is employed as an ingredient of our compositions it is usually advantageous to employ with it a lead scavenger. Preferred types and amounts of such scavengers are those disclosed in U.S. Patents 2,398,281; 2,479,900; 2,479,901; 2,479,902; 2,479,903 and 2,496,983, particularly halohydrocarbons such as bromohydrocarbons and chlorohydrocarbons.

We find it very convenient to utilize antiknock fluids which consist of organolead antiknock agents and cyclo-matic compounds having the general formula MA_xB_y , wherein M is manganese, A is a cyclo-matic radical, preferably a cyclopentadienyl hydrocarbon radical, B is carbon monoxide, x is one and y is three. In other words, we contemplate as part of our invention antiknock fluids which comprise organolead antiknock agents and cyclopentadienyl manganese tricarbonyls of the type described hereinabove. Such fluids preferably, but not necessarily, also contain scavenging agents such as the type referred to hereinabove, particularly halohydrocarbon scavengers such as bromohydrocarbons and chlorohydrocarbons. Among the preferred types and amounts of scavengers are those described in U.S. Patent 2,398,281.

Use of such antiknock fluids in addition to resulting in great convenience in storage, handling, transportation, blending with fuels, and so forth also are unexpectedly potent concentrates which serve the multipurpose functions of being useful as antiknocks, deposit modifiers, valve corrosion inhibitors, wear reducers and the like. The fluids are also found to possess a surprising degree of inherent stability.

In such fluids we prefer to use hydrocarbon lead compounds such as tetraphenyllead, tetratolyllead and particularly tetraalkyllead compounds such as tetramethyllead, tetraethyllead, and tetrapropyllead and the like.

We also particularly prefer to employ in our fluids cyclopentadienyl manganese tricarbonyl compounds which are liquid at room temperature. An example of such a compound is methylcyclopentadienyl manganese tricarbonyl.

In our fluid compositions the weight ratio of manganese-to-lead can vary from about 0.1 gram of manganese to 8 grams of lead or even 0.01 gram of manganese to 8 grams of lead on the one hand to about 6 grams of manganese to about 1 gram of lead on the other hand. Best results are obtained when this ratio varies from about 0.1 gram of manganese to 8 grams of lead to about 3 grams of manganese to 2 grams of lead. The amount of scavenger employed in our fluids usually ranges from about 1 theory to about 3 theories based on the amount of lead present. However, amounts as low as 0.1 theory can be used.

The following examples illustrate typical fluid compositions of the invention.

EXAMPLE XI

Tetraethyllead and methylcyclopentadienyl manganese tricarbonyl are admixed so that the ratio is 8 grams of lead as tetraethyllead present for every 0.1 gram of manganese present as methylcyclopentadienyl manganese tricarbonyl. This composition is found to possess superior antiknock and deposit modifying properties.

EXAMPLE XII

To the composition of Example XI is added ethylene dibromide in amount such that there is one theory of scavenger present based upon the amount of tetraethyllead.

EXAMPLE XIII

Tetramethyllead and ethylcyclopentadienyl manganese tricarbonyl are admixed in amount such that there is one gram of lead present for every 6 grams of manganese in the fluid.

EXAMPLE XIV

To the composition of Example XIII is added a 2 to 1 mole mixture of ethylene dichloride and ethylene dibromide such that a total scavenger of 1.5 theories based on lead is present.

EXAMPLE XV

An additive fluid consisting of 1 gram of lead as tetraethyllead and 1 gram of manganese as methylcyclopentadienyl manganese tricarbonyl is prepared. This mixture is found to give superior results and gives even better results when it is blended with dibromotoluene as scavenger to give a total scavenger of 3 theories based on the amount of tetraethyllead present.

The cyclopentadienyl manganese tricarbonyl additives of this invention may be mixed with antioxidants, such as alkylated phenols and amines, metal deactivators, phosphorus compounds, antiknock agents, such as amines as well as the alkyllead compounds mentioned above, anti-rust and anti-icing agents, and wear inhibitors, may also be added to the antiknock composition or fuel containing the same.

As one such embodiment, we provide antiknock fluids and fuels which contain an organolead antiknock agent, such as tetraethyllead, a cyclopentadienyl manganese tricarbonyl supplementary antiknock agent, such as methylcyclopentadienyl manganese tricarbonyl and a gasoline-soluble compound of a group V-A element having atomic number 15-51, such as phenyl dimethyl phosphate.

It has been found that antiknock fluid and gasoline compositions falling within the scope of this invention and containing the aforementioned group V-A compounds provide significant benefits in terms of improved exhaust valve life. For example, in a modern V-8 high compression automobile engine run on a passenger car cycling schedule, use of gasoline containing 3.0 ml. per gallon (3.18 grams of lead per gallon) of tetraethyllead as 62-Mix gave an exhaust valve life of 300 hours under the test conditions employed. When the same engine was run on the same cycle with the same fuel except that it contained additionally 0.15 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl the life of the exhaust valve was reduced to less than 100 hours. However, when the same engine was again run on the same cycle with the identical manganese-containing fuel except that it additionally contained 0.1264 gram per gallon of phosphorus as dimethyl monoresyl phosphate the life of the exhaust valve was increased to 450 hours.

The gasoline-soluble compound of a group V-A element (from the table of Deming, "Fundamental Chemistry," second edition, John Wiley and Sons), of atomic number 15-51 is, in other words, a gasoline-soluble compound of phosphorus, arsenic or antimony. The phosphorus compounds are preferred because of availability and potency.

Among the phosphorus compounds useful in the present compositions are both inorganic and organic compounds. Typical inorganic phosphorus compounds include phosphonitrilic dichloride, phosphorus sesquisulfide, and the like. Typical organic compounds include the trivalent esters of phosphorus such as triphenyl phosphite, triethyl phosphite, diethyl phosphite, trimethyl phosphite, tri-sec-octyl phosphite, tri(β -chloroethyl)phosphite, and the like.

Another suitable, and indeed preferred, class includes the pentavalent esters of phosphorus acids. Examples of these both in the alkyl and aryl categories include trimethyl phosphate, trimethyl thionophosphate, triethyl phosphate, tributyl phosphate, triisooamyl phosphate, dimethylphenyl phosphate, tri(β -chloropropyl)thionophosphate, tricresyl phosphate, dimethyl monoxyl phosphine, etc. Dimethyl monoaryl phosphates such as dimethyl phenyl phosphate are the most preferred compounds of group V-A elements as they cause substantially no destruction of tetraethyllead effectiveness.

Among the phosphorus compounds containing carbon-to-phosphorus bonds, we prefer to use the phosphines such as trimethyl phosphine, triethyl phosphine, trioctyl phosphine, triphenyl phosphine and the like. Tertiary phosphine oxides such as trimethyl phosphine oxide, tripropyl phosphine oxide, triphenyl phosphine oxide and analogous phosphine sulfides such as triisobutyl phosphine sulfide and tribenzyl phosphine sulfide are also useful. Another class of suitable phosphorus compounds include the phosphonates such as diethyl methane phosphonate, diethyl propane phosphonate, dibutyl isoprene phosphonate, etc.

Various more complex phosphorus compounds such as the P_2S_5 -active hydrogen compound reaction products, disclosed in U.S. Patents 2,794,718; 2,794,719; 2,794,715; 2,794,717; 2,794,720; 2,794,721; 2,794,713; 2,794,722; 2,794,714; and 2,794,716, can also be employed, as can nitrogen-containing compounds such as aminophosphates, amidophosphites and sulfur analogs thereof. Our preferred group V-A compounds are liquid materials containing 3-30 carbon atoms, most usually phosphates.

The arsenic and antimony compounds used in the practice of this invention are in general similar to the phosphorus compounds outlined above. Among those which we prefer to use are the arsines such as trimethyl arsine and triphenyl arsine, the stibines such as triethyl stibine and tritolyl stibine and also the glycol complexes of various arsenic acids such as those described in U.S. Patent 2,795,551.

We have further established that the exact nature of the group V-A compound is immaterial so long as it is a gasoline-soluble compound of a group V-A element of atomic number 15-51. It is the combustion product of the group V-A element which functions to improve exhaust valve life in our compositions and since the compounds of any given group V-A element are always converted to the same combustion product or products the exact nature of the additive, so long as it is gasoline-soluble, is not critical.

In many types of operation it is desirable to augment the above described compositions by use of a scavenger for the organolead antiknock agent. These scavengers are customarily halogenated organic compounds of the type described hereinbefore.

We have found that best results are obtained when we blend our fluids into gasoline such that the gasoline contains between 0.02 and 13.2 grams per gallon of lead as organolead antiknock agent. When tetraethyllead is the organolead agent this corresponds to a concentration of approximately 0.02 to 13.9 ml. per gallon. The amount of cyclopentadienyl manganese tricarbonyl compounds used customarily ranges between 0.015 and 10.0 grams of manganese per gallon, although it is seldom necessary to go beyond 6.0 grams per gallon of manganese. The amount of group V-A element used ordinarily ranges between 0.0004 gram per gallon and 2.63 gram per gallon. When the element is phosphorus we ordinarily use 0.0004-0.67 gram per gallon; with arsenic the corresponding figures are 0.001-1.62 gram per gallon and with antimony 0.016-2.63 gram per gallon.

Translating the above figures into antiknock fluids it can be seen that we ordinarily blend our fluids so that for every part by weight of lead present as organolead antiknock agent there is present 0.0011 to 500 parts by weight

of manganese as a cyclopentadienyl manganese tricarbonyl and 0.00003 to 132 parts by weight of group V-A element as a gasoline-soluble compound thereof. Thus, the ratio of manganese-to-lead in our fluids and fuels ranges from 1/880 to 500/1.

While the above amounts are indicative of the broad ranges of compositions which we employ in this embodiment, we ordinarily prefer to use considerably narrower ranges. For example, in most of our compositions we find it preferable to use more organolead compound, on a weight-of-metal basis, than organomanganese compound, preferably such that for every part of lead present as organolead compound there are present 0.015-0.33 part by weight of manganese as a cyclopentadienyl manganese tricarbonyl. With such proportions we achieve optimum antiknock response and valve life improvement.

Moreover, we get best results when we control the amount of group V-A element according to the amount of lead present. In general, best results are obtained when the amount of group V-A element present is equivalent to 0.2-0.5 theory based on the lead present as organolead antiknock agent, although we can use the group V-A element in amounts ranging from 0.01-1.5 theories. In terms of parts by weight this amounts to 0.02-0.2 part of group V-A element as a gasoline-soluble compound thereof for every part of lead present as organolead antiknock agent. When the group V-A element is phosphorus the amount of this element present is preferably 0.02-0.05 part per part of lead.

(NOTE.—It is convenient also to describe the amount of group V-A compound used in terms of theories as has been done the preceding paragraph. One theory of group V-A additive is that amount of additive which provides the exact amount of group V-A element necessary to react quantitatively with the lead present as organolead antiknock agent to convert it to lead phosphate, arsenate or antimonate. This amount of additive is equivalent to two atoms of group V-A element for every three atoms of lead present and in the case of phosphorus is equivalent to 0.1 gram of phosphorus for every gram of lead present.)

EXAMPLE XVI

By blending together 6.34 parts of tetraethyllead, 2.0 parts of cyclopentadienyl manganese tricarbonyl and 0.316 part of tris(β -chloropropyl)thionophosphate a suitable fluid falling within the scope of the present invention is obtained.

EXAMPLE XVII

To a fuel containing 0.02 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 tricresyl phosphate, is added phenylcyclopentadienyl manganese tricarbonyl 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.

EXAMPLE XVIII

To 1000 gallons of a gasoline made up of 39.1 percent paraffins, 21.1 percent olefins, 17.1 percent aromatics, 22.8 percent naphthenes, and having an end point of 426° F., a gravity of 61.4° API and a vapor pressure of 11.7 p.s.i., and containing 3.0 ml. of tetraethyllead as 62-Mix, is added methylcyclopentadienyl manganese tricarbonyl in amount equal to 0.25 gram of manganese per gallon and 0.4 theory of phosphorus as dimethyl monotoyl phosphate. To two more batches of this same leaded fuel is added indenyl manganese tricarbonyl to a manganese concentration of 0.1 gram per gallon and of 6.0 gram per gallon respectively.

EXAMPLE XIX

Example XVIII is repeated in its entirety except that dimethyl phenyl phosphate is used instead of dimethyl monotoyl phosphate.

EXAMPLE XX

A fluid consisting of 57.52 parts of tetraethyllead, (blended with 17.6 parts of ethylene dichloride and 16.7 parts of ethylene dibromide), 6.97 parts of methylcyclopentadienyl manganese tricarbonyl, and 4.97 parts of trimethyl phosphate is prepared. This is added to gasoline E in amounts so that there is present 3 ml. of tetraethyllead per gallon of the gasoline. The gasoline composition of this example can also be prepared by adding the phosphorus compound separately to the fuel already containing the lead, manganese and halo hydrocarbon compounds.

In an additional embodiment, we oxidatively stabilize gasoline containing a cyclopentadienyl manganese tricarbonyl antiknock agent, by incorporating in such fuel, in quantity sufficient to inhibit oxidative deterioration, an N,N'-dialkyl-p-phenylene diamine. The diamine is preferably one in which the alkyl groups are lower alkyl groups—i.e., each contain up to about 6 carbon atoms. N,N'-di-sec-butyl-p-phenylene diamine is especially effective and particularly preferred.

To illustrate the effectiveness of such stabilizers, two samples of a gasoline were each formulated with 3.18 grams of lead per gallon as tetraethyllead (with 0.5 theory of ethylene dibromide and 1.0 theory of ethylene dichloride) and 0.5 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl. To one of the samples was added 0.022 weight percent of N,N'-di-sec-butyl-p-phenylenediamine; the other was left unstabilized. The two samples were then stored at 110° F. and analyzed periodically to determine their content of gum and soluble alkyllead salts. The formation of these materials is proof that decomposition of the fuel has taken place. Therefore, the relative stabilities of the test fuels were directly measured by determining the length of time required to form 7 milligrams of gum per 100 milliliters of fuel and 3 milligrams of lead as soluble alkyllead salts per 100 milliliters of fuel. The longer the time required to form these amounts of decomposition products, the more stable was the fuel composition. The unstabilized fuel formed 7 mg. of gum/100 ml. of fuel in 7 weeks (as measured by ASTM Test Procedure D-381), whereas the stabilized fuel took more than 16 weeks. The time for the unstabilized fuel to form 3 mg. soluble alkyllead salts/100 ml. of fuel (determined by extracting samples of the fuel with an ammonia-ammonium acetate solution and assaying the amount of lead so extracted) was 6 weeks, whereas the stabilized gasoline took over 16 weeks.

The N,N'-dialkyl-p-phenylene diamine concentrations used in this embodiment range from about 0.002 to about 0.1 percent based on the weight of the fuel. In some cases it is advantageous to use amounts ranging up to about 0.2 percent or more, particularly where the base fuel tends to deteriorate rapidly even in the absence of the manganese ingredient. It is also desirable to use relatively high concentrations of the diamine when the fuel contains relatively high concentrations of cyclopentadienyl manganese tricarbonyls. Generally speaking, it is desirable to use diamine concentrations ranging from about 0.0002 to about 0.05 weight percent. Although in most cases no more than about 0.02 weight percent is needed.

Typical N,N'-dialkyl-p-phenylene diamine used in this embodiment include N,N'-dimethyl-p-phenylene diamine; N,N'-diethyl-p-phenylene diamine; N,N'-dipropyl-p-phenylene diamine; N,N'-diisopropyl-p-phenylene diamine; N,N'-dibutyl-p-phenylene diamine; N,N'-diisobutyl-p-phenylene diamine; N,N'-di-tert-butyl-p-phenylene diamine; the various N,N'-diamyl-p-phenylene di-

amines; and N,N'-dihexyl-p-phenylene diamine; N-methyl-N'-hexyl-p-phenylene diamine; N-isopropyl-N'-sec-butyl-p-phenylene diamine; and the like. On a cost-effectiveness basis, N,N'-di-sec-butyl-p-phenylene diamine is especially preferred.

EXAMPLE XXI

To 1000 gallons of a commercial gasoline having a gravity of 59.0° API, an initial boiling point of 98° F., and a final boiling point of 390° F. are added 3.18 grams per gallon of lead as tetraethyllead, 0.6 theory (based on the lead) of bromine as ethylene dibromide, 1.0 theory (based on the lead) of chlorine as ethylene dichloride, 0.25 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl and 0.015 weight percent (based on the gasoline) of N,N'-di-sec-butyl-p-phenylene diamine. The resultant fuel possesses enhanced fuel stability characteristics.

A further embodiment of the invention comprises stabilization against oxidative deterioration of the cyclopentadienyl manganese tricarbonyl-containing gasolines by the inclusion in such fuels, in quantity sufficient to inhibit oxidative deterioration, of a p-aminophenol. The p-aminophenol is preferably one in which the amino nitrogen is substituted with a lower alkyl group—i.e., an alkyl group containing up to about 6 carbon atoms. The p-butyl aminophenols are especially effective and particularly preferred.

In oxidative stability tests conducted as described hereinabove, a gasoline containing 3.18 grams of lead per gallon as tetraethyllead (with 1.0 theory of ethylene dichloride and 0.5 theory of ethylene dibromide) and 0.5 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl formed 7 mg. gum/100 ml of fuel in 7 weeks and 3 mg. soluble alkyllead salts/100 ml. of fuel in 6 weeks. In contrast, the corresponding times for the identical fuel additionally containing 0.022 weight percent of p-n-butyl aminophenol were over 16 weeks in both instances.

The p-aminophenol concentrations used in this embodiment range from about 0.002 to about 0.1 percent based on the weight of the fuel. In some cases it is advantageous to use amounts ranging up to about 0.2 percent or more, particularly where the base fuel tends to deteriorate rapidly even in the absence of the manganese ingredient. It is also desirable to use relatively high concentrations of the aminophenol when the fuel contains relatively high concentrations of cyclopentadienyl manganese tricarbonyls. Generally speaking, it is desirable to use aminophenol concentrations ranging from about 0.0002 to about 0.05 weight percent, although in most cases no more than about 0.02 weight percent is needed.

Typical p-aminophenols used in the practice of this invention include p-aminophenol, p-methyl aminophenol, p-ethyl aminophenol, p-propyl aminophenol, p-isopropyl aminophenol, the p-butyl aminophenols, the p-amyl aminophenols, the p-hexyl aminophenols, p-amino-o-cresol, p-ethyl amino-m-cresol, p-amino-2,6-di-tert-butyl phenol, p-sec-butyl amino-2-methyl-6-isopropyl phenol, and the like. Particularly preferred on a cost-effectiveness basis are the p-butyl aminophenols, i.e., p-n-butyl aminophenol, p-isobutyl aminophenol, p-sec-butyl aminophenol, and p-tert-butyl aminophenol. Generally speaking, the stabilizers used in this invention are monohydric phenols which contain a single amino or alkyl amino group in the para position with respect to the phenolic hydroxyl group, and which contain in the molecule a total of from 6 to 20 carbon atoms.

EXAMPLE XXII

To 1000 gallons of a commercial gasoline having a gravity of 59.0° API, an initial boiling point of 98° F., and a final boiling point of 390° F. are added 3.18 grams per gallon of lead as tetraethyllead, 0.6 theory (based on the lead) of bromine as ethylene dibromide, 1.0 theory

(based on the lead) of chlorine as ethylene dichloride, 0.25 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl and 0.015 weight percent (based on the gasoline) of p-butyl aminophenol. The resultant fuel possesses enhanced fuel stability characteristics.

In the embodiment described hereinabove wherein the cyclopentadienyl manganese tricarbonyl-containing gasoline additionally contains a sulfur-containing material, the sulfur containing material is preferably selected from the class consisting of elemental sulfur, carbon disulfide, and organic sulfur-containing compounds selected from the group consisting of sulfides, disulfides, polysulfides, thiophenes and mercaptan compounds, said compounds characterized by containing up to about 12 carbon atoms in the molecule and containing only sulfur, carbon and elements selected from the group consisting of hydrogen, oxygen, nitrogen, chlorine and phosphorus.

Data illustrating improvement in spark plug life brought about through use of this embodiment are described earlier in this specification.

Among the sulfur-containing materials used in this embodiment are elemental sulfur itself, sulfides such as dimethyl sulfide, diethyl sulfide, methylethyl sulfide and the like. We prefer to use the sulfides having the formula, RSR_1 , where R and R_1 are organic radicals containing no more than about 12 carbon atoms and are selected from the class consisting of alkyl, cycloalkyl, aralkyl, aryl and alkaryl radicals. We can also use disulfides such as diethyl disulfide, ethylbenzyl disulfide, and in general, compounds having the formula, $RSSR_1$, where R and R_1 are organic radicals containing no more than 12 carbon atoms and are selected from the class consisting of alkyl, cycloalkyl, aralkyl, aryl and alkaryl radicals. We can also use sulfoxides such as phenyl sulfoxide, diethyl sulfoxide; sulfones such as ethyl sulfone, phenyl sulfone, ethylphenyl sulfone; polysulfides such as ethyltrisulfide, ethylphenyltrisulfide and the like. Other sulfur compounds that are usable are the carbon sulfides such as carbon disulfide, carbon monosulfide, and carbon subsulfide. We can also use mercaptan compounds such as ethyl mercaptan, propyl mercaptan, benzyl mercaptan and the like. The preferred mercaptan compounds have the formula RSH wherein R is an organic radical containing no more than about 12 carbon atoms and is selected from the class consisting of alkyl, cycloalkyl, aralkyl, aryl and alkaryl radicals. Additional compounds usable in our compositions are mercaptans such as diethylmercaptopropane, bis(benzylmercapto)methane; mercaptols such as dibenzyl mercaptol; thiones such as 3-pentanethione, 3-butanethione; thioacetophenone; polythiones such as 2,4-pentadithione; cyclothiones such as cyclohexanethione, pyridinethione, and the like.

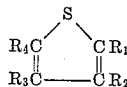
Additional compounds we can use include thioesters such as di-sec-butylphosphonothionate and bis(2-ethylhexyl) xylylphosphoramidothionate.

Still other compounds that we can use are sulfur organic acids. Examples are sulfinic acids such as propane sulfinic acid, benzene sulfinic acid. We can also use the esters formed from these acids such as the methyl, ethyl, propyl, and benzyl esters. We can also use organic sulfates, sulfides, sulfones and sulfoxides. Examples are the ethyl, propyl, and phenyl compounds.

Our sulfur-containing compounds may also contain a halogen, especially bromine and chlorine. Such compounds may be especially desirable, for not only do they provide the essential sulfur, but also the halogen may serve as a scavenging agent. Examples of these compounds are tri(2-chloro-1-methylethyl) phosphorothionate, tris(2-chloro-ethyl) phosphorothionate, and the like.

Still other sulfur materials that are usable in the compositions of this invention are heterocyclic compounds. We can use thiophenes, including thiophene itself and substituted thiophenes such as hydroxythiophene, methylhydroxythiophene, ethylthiophene, benzylthiophene,

aminothiophene, acetylthiophene, thiophenethiol and thiophenedithiol. We can also use compounds containing a multiple thiophene ring such as thieno[2,3-b]thiophene. The preferred thiophene compounds have the formula



wherein R_1 , R_2 , R_3 and R_4 are selected from the group consisting of hydrogen and organic radicals containing up to about 8 carbon atoms selected from the class consisting of alkyl, cycloalkyl, aralkyl, aryl and alkaryl radicals.

Further, we can use sulfur-containing naphthenes such as methyl-, trimethyl-, ethyl-, thionaphthenes. Other heterocyclic sulfur compounds usable in the compositions of our invention are isothionaphthenes and dibenzothiophenes.

Additional sulfur-containing material that we can use are thiadiazoles such as the methyl, ethyl, and phenyl compounds. Moreover, we can use the benzothiadiazoles and benzisothiazoles.

Although we can use any of the compounds enumerated above, singly or admixed, we most prefer to use sulfur-containing materials whose boiling points are close to or within the boiling range of gasoline; viz., 70-475° F. Examples of such compounds are the sulfides, disulfides, polysulfides, mercaptans, thiones and others containing up to about 12 carbon atoms in the molecule. Our most preferred sulfur compounds are the thiophenes and carbon sulfides. In many cases, thiophene itself has given outstanding results and of the thiophenes is the preferred compounds. With many fuels best results have been obtained by using carbon disulfide as the added sulfur compound and, hence, this is one of our most preferred materials. Although we prefer to use our sulfur compounds singly, we can use mixtures of any of the above enumerated compounds.

Although our compositions may contain from about 0.005 to about 0.3 percent by weight sulfur, there is ordinarily no great advantage in using concentrations much in excess of about 0.10 percent by weight sulfur. Best usage occurs when the concentration is at least 0.009 percent by weight and in many fuels at least 0.015 percent by weight. We especially prefer to use from about 0.015 to about 0.065 weight percent sulfur in our compositions.

Our sulfur compounds may be added to fuels containing naturally occurring sulfur compounds. Indeed, most gasolines ordinarily contain varying amounts of sulfur. In such cases, only that amount of sulfur required to bring the total sulfur content to the desired concentration need be added. Some gasolines may naturally contain the total amount of the desired sulfur. For these fuels, we need add only the cyclomatic manganese compound and, optionally, a tetraalkyllead compound to obtain our compositions.

EXAMPLE XXIII

The base fuel of this example comprises a commercial type fuel composed of 30 percent catalytic reformate, 20 percent alkylate, 20 percent catalytically cracked material, 15 percent polymer, and 15 percent straight run material and containing 0.002 weight percent sulfur. To this fuel is added 0.1 gram of lead per gallon as tetraethyllead, 0.5 theory of ethylene dibromide (based on the lead content), 1.0 theory of ethylene dichloride, 0.3 theory of phosphorus as trimethyl phosphate, and 6.0 grams per gallon of manganese as methylcyclopentadienyl manganese tricarbonyl and 0.007 weight percent sulfur as thiophene. This fuel has the attributes of long spark plug life and resistance to surface ignition and rumble.

Additional examples of this embodiment are presented below. In each case the gasoline is a highly saturated fuel comprising 40 percent alkylate, 10 percent isomerate, 15

percent straight run material and 25 percent catalytically cracked material, and 10 percent catalytic reformate.

the clear fuel. The synergistic mixture had a research octane number 2.4 units higher than expected.

Example	Cyclopentadienyl radical CyMn(CO) ₃	Concentration, g. Mn/gal. fuel	Organolead Anti-knock Agent	Concentration, g. Pb/gal. fuel	Sulfur-containing material	Concentration, wt. percent S in fuel
XXIV	C ₅ H ₅ *	0.5	None	None	Carbon Disulfide	0.015
XXV	CH ₃ C ₅ H ₄ *	0.02	TEL	3.18	Elemental sulfur	0.024
XXVI	C ₆ H ₅	1.0	TML	3.60	Dimethylsulfide	0.10
XXVII	C ₆ H ₅ *	0.075	TEL	1.05	Diphenyl disulfide	0.15
XXVIII	C ₂ H ₅ C ₅ H ₄ *	2.5	None	2.50	Benzyl mercaptan	0.3
XXIX	CH ₃ C ₅ H ₄	0.5	50 percent TML— 50 percent TEL	2.50	Ethyl phenyl trisulfide	0.05
XXX	C ₅ H ₅	0.25	TEL	4.0	Tris(2-chloro-1-methyl-ethyl)phosphorothionate	0.07

*C₅H₅=cyclopentadienyl; CH₃C₅H₄=methylcyclopentadienyl; C₆H₅=indenyl; C₂H₅C₅H₄=ethylcyclopentadienyl.
TEL=tetraethyllead; TML=tetramethyllead.

An important benefit of the use of combinations of cyclopentadienyl manganese tricarbonyl antiknocks and organolead antiknocks in accordance with this invention is that such combinations are synergistic in their antiknock activity.

For example, when small amounts of manganese as a cyclopentadienyl manganese tricarbonyl compound are used in conjunction with from one to about six grams of lead per gallon as an organolead compound, a synergistic effect is obtained in terms of the increase in octane quality of the gasoline. This effect is realized at manganese concentrations up to about 15 percent of the total metal concentration of the fuel, and is observed at concentrations as low as 0.03 gram of manganese per gallon, or even lower amounts of manganese, such as the amounts illustrated hereinabove, in fuels containing at least one gram of lead as an organolead compound, such as tetraethyllead, per gallon.

The increase in octane number obtained by replacing a small amount of lead with an equal amount of manganese as a cyclopentadienyl manganese tricarbonyl compound is totally unexpected. That is, a great percentage of the increase which is obtainable from a complete replacement of lead with a cyclopentadienyl manganese tricarbonyl is realized with the first incremental amounts of the latter. Thus, a mixture of 95 percent lead and five percent manganese as a cyclopentadienyl manganese tricarbonyl affects as much as 50 percent of the improvement in octane quality which can be realized with a complete replacement of lead with such a compound.

For example, a commercial fuel having an octane number of 90.6 when three grams of lead as tetraethyllead have been added thereto and an octane number of 96.6 when three grams of manganese as methylcyclopentadienyl manganese tricarbonyl have been added thereto has an octane number of 93.6 when 2.85 grams of lead as tetraethyllead and 0.15 gram of manganese as methylcyclopentadienyl manganese tricarbonyl have been added to the fuel. Thus, one-half of the possible improvement to be realized upon replacing the lead with an identical amount of manganese as methylcyclopentadienyl manganese tricarbonyl has been realized upon replacing only five percent of the lead with manganese as methylcyclopentadienyl manganese tricarbonyl. As another example, the research octane number of a hydrocarbon fuel of the gasoline boiling range was found to be 72.0 when it contained no antiknock agent. When 2.36 ml./gallon of tetraethyllead was added, the research octane number was 85.2, a gain of 13.2 octane numbers. The corresponding number when the fuel contained 0.25 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl (but no lead) was 76.4, or a gain of 4.4 over the additive-free fuel. The expected research octane number for the fuel containing the combination of 2.36 ml. tetraethyllead per gallon and 0.25 gram per gallon of manganese was accordingly 17.6 (13.2+4.4). As actually determined, however, the research octane number was 92.0, which is a gain of 20 octane numbers over

Other important objects of this invention are accomplished by providing compositions consisting of liquid hydrocarbon crankcase lubricating oil containing a cyclopentadienyl manganese tricarbonyl compound in amount sufficient to improve the operating characteristics of a spark ignition internal combustion engine.

It has also been found that when a cyclopentadienyl manganese tricarbonyl compound is added to the crankcase lubricating oil of an internal combustion engine, a drastic and rapid decrease in the octane requirement of the engine takes place. This is believed to be due to the fact that the manganese compound enters the cylinders of the engine either as a vapor or in the oil film on the cylinder walls. Thus, the objects of this invention are also accomplished by providing a lubricating oil for internal combustion engine which oil contains a cyclopentadienyl manganese tricarbonyl compound in amount sufficient to reduce the octane requirement of the fuel used in the engine.

The antiknock effect produced by adding a cyclopentadienyl manganese tricarbonyl to crankcase lubricating oil is illustrated by the following: A single cylinder CFR L-head test engine was found to have a steady state octane requirement of 78 when used with ordinary multiviscosity light solvent refined crankcase lubricating oil. When 2.5 percent manganese as methylcyclopentadienyl manganese tricarbonyl was added to the oil, the octane requirement dropped to 34; a reduction of over 56 percent in the octane number of the gasoline required to give knock-free performance of this engine. Thus, sufficient methylcyclopentadienyl manganese tricarbonyl was introduced into the engine to raise the octane number of a gasoline by 44 octane number units.

It has also been found that the lubricity of the aforesaid lubricating oils may be greatly enhanced by addition thereto of the cyclopentadienyl manganese tricarbonyl compound. This is illustrated by the results of tests carried out in the four-ball wear machine, which test is described in the Larson et al. paper in "Transactions of the A.S.M.E.," January 1945, pages 45-50. Typical results are shown by the following examples.

EXAMPLE XXXI

A mid-Continent solvent-extracted mineral oil, not containing a cyclopentadienyl manganese tricarbonyl, was run in the four-ball wear machine utilizing one-half inch in diameter SAE 52-100 steel balls, a speed of 570 r.p.m. for two hours at a load of 10 kilograms. Following the test, the balls were disassembled and the average scar diameter on the lower three balls was measured and found to be 0.62 millimeter.

EXAMPLE XXXII

The lubricating oil of the preceding example, containing 5 percent of methylcyclopentadienyl manganese tricarbonyl, was run in the four-ball wear machine under the same test conditions utilized in Example XXXI. Following the test, the balls were disassembled and the aver-

age scar diameter on the lower three balls was measured and found to be only 0.28 millimeter.

When used for the purpose of increasing lubricity, the cyclopentadienyl manganese tricarbonyl will ordinarily be present in concentration ranging from 0.1 to about 10 percent by weight of the base lubricating oil. When used for the purpose of reducing octane requirement, concentrations as low as those corresponding to about 0.03 weight percent manganese in the lubricating oil are useful.

The lubricating oils used in the practice of this invention include those fractions or blends of fractions from mineral oils which are used for lubricating purposes in the crankcase of an internal combustion engine. Lubricating oil stock is usually considered to include all the distillate obtainable from crude oils after the lower boiling fractions and gas oils have been expelled, as well as some of the residues that are left in the still when non-asphaltic crudes are distilled.

Generally lubricating oils are made from distilled fractions of a crude, but often those distilled fractions are combined with refined residuum, such as bright stocks, to yield oils having excellent lubricating qualities.

In addition to the cyclopentadienyl manganese tricarbonyl compound, the lubricating oils of this invention may contain other additives. These other additives may include for example viscosity index improvers, detergents, corrosion inhibitors, metal deactivators, rust inhibitors, color stabilizers, pour depressants, emulsifiers, dyes, etc.

We claim:

1. Gasoline containing a cyclopentadienyl manganese tricarbonyl in an amount sufficient to improve the antiknock characteristics of said gasoline.

2. Gasoline containing an amount of tetraethyllead sufficient to increase its antiknock effectiveness and also containing a minor amount of cyclopentadienyl manganese tricarbonyl sufficient to further increase its antiknock effectiveness.

3. As a new composition of matter a fuel for internal combustion engines consisting essentially of gasoline containing from about 0.05 to 6.0 grams per gallon of manganese as a compound having a cyclopentadienyl group coordinated with manganese, said cyclopentadienyl group having from 5 to 13 carbon atoms, the compound being stabilized by additional coordination with three carbonyl groups, each of which donates two electrons so that the sum of all coordinated electrons and the atomic number of the manganese is equal to the atomic number of the next higher rare gas.

4. As a new composition of matter a fuel for internal combustion engines consisting essentially of gasoline containing from 0.1 to about 4.0 grams per gallon of manganese as a cyclopentadienyl manganese tricarbonyl compound which is liquid at ordinary temperatures, wherein the manganese has the electronic configuration of the next higher rare gas.

5. The composition of claim 4 wherein the liquid cyclopentadienyl manganese tricarbonyl compound is methylcyclopentadienyl manganese tricarbonyl, wherein the manganese has the electronic configuration of the next higher rare gas.

6. As a new composition of matter, a fuel for internal combustion engines consisting essentially of gasoline containing from about 0.05 to 6.0 grams per gallon of manganese as a cyclopentadienyl manganese tricarbonyl compound wherein the cyclopentadienyl group contains from 5 to 13 carbon atoms, wherein the manganese has the electronic configuration of the next higher rare gas, and from about 1 to 8 grams per gallon of lead as hydrocarbon lead antiknock agent.

7. The composition of claim 6 wherein said cyclopentadienyl manganese tricarbonyl compound is methylcyclopentadienyl manganese tricarbonyl and the hydrocarbon lead antiknock agent is tetraethyllead.

8. As a new composition of matter an additive fluid composition consisting essentially of a hydrocarbonlead

antiknock agent and a cyclopentadienyl manganese tricarbonyl compound having from 5 to 13 carbon atoms, wherein the manganese has the electronic configuration of the next higher rare gas and wherein the weight ratio of lead-to-manganese is from about 160 to 1 to about 1 to 6.

9. As a new composition of matter an additive fluid composition consisting essentially of tetraethyllead, a halohydrocarbon scavenger therefor and methylcyclopentadienyl manganese tricarbonyl wherein the weight ratio of lead-to-manganese is from about 160 to 1 to about 1 to 6.

10. Gasoline containing an amount of tetramethyllead sufficient to increase its antiknock effectiveness and also containing a minor amount of methylcyclopentadienyl manganese tricarbonyl sufficient to further increase its antiknock effectiveness.

11. The composition of claim 8 wherein said hydrocarbonlead antiknock agent is tetramethyllead and said cyclopentadienyl manganese tricarbonyl compound is methylcyclopentadienyl manganese tricarbonyl.

12. A liquid hydrocarbon crankcase lubricating oil containing a cyclopentadienyl manganese tricarbonyl compound in amount sufficient to improve the operating characteristics of a spark ignition internal combustion engine.

13. The composition of matter of claim 12 wherein the compound is methylcyclopentadienyl manganese tricarbonyl.

14. As a new composition of matter an antiknock fluid which consists essentially of an organolead antiknock agent, a cyclopentadienyl manganese tricarbonyl antiknock agent and a gasoline-soluble organic compound of a group V-A element of atomic number 15-51, said organic compound containing 3-30 carbon atoms and being present in relative amounts such that for every part by weight of lead as the organolead antiknock agent, there are 0.0011 to 500 parts by weight of manganese as the cyclopentadienyl manganese tricarbonyl and 0.00003 to 132 parts by weight of group V-A element of atomic number 15-51 as the gasoline-soluble compound thereof.

15. The composition of claim 14 wherein said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl manganese tricarbonyl and said element is phosphorus.

16. The composition of claim 14 wherein said group V-A compound is dimethyl monoaryl phosphate.

17. The composition of claim 14 wherein said organolead antiknock agent is tetraethyllead, said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl manganese tricarbonyl and said organic compound of a group V-A element is trimethylphosphate.

18. As a new composition of matter, fuel for spark ignition internal combustion engines which consists essentially of gasoline containing an organolead antiknock agent, a cyclopentadienyl manganese tricarbonyl antiknock agent and a gasoline-soluble organic compound of a group V-A element of atomic number 15-51, said organic compound containing 3-30 carbon atoms and being present in amounts such that for every part by weight of lead as the organolead antiknock agent there is present 0.0011 to 500 parts by weight of manganese as the cyclopentadienyl manganese tricarbonyl and 0.00003 to 132 parts by weight of group V-A element of atomic number 15-51 as the gasoline soluble compound thereof.

19. The composition of claim 18 wherein said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl manganese tricarbonyl and said element is phosphorus.

20. The composition of claim 18 wherein said group V-A compound is dimethyl-phenyl phosphate.

21. The composition of claim 18 wherein said organolead antiknock agent is tetraethyllead, said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl

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manganese tricarbonyl and wherein said organic compound of a group V-A element is trimethylphosphate.

22. Gasoline containing a small amount, sufficient to accelerate deterioration thereof, of a cyclopentadienyl manganese tricarbonyl antiknock agent and additionally containing, in quantity sufficient to inhibit such deterioration, a small amount of a p-alkylaminophenol in which said alkyl group contains up to about 6 carbon atoms.

23. The composition of claim 22 wherein said phenol is p-butylaminophenol and said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl manganese tricarbonyl.

24. Gasoline containing a small amount, sufficient to accelerate deterioration thereof, of a cyclopentadienyl manganese tricarbonyl antiknock agent and additionally containing, in quantity sufficient to inhibit such deterioration, a small amount of an N,N'-dialkyl-p-phenylene diamine in which each alkyl group contains up to about 6 carbon atoms.

25. The composition of claim 24 wherein said diamine is N,N'-di-sec-butyl-p-phenylene diamine and said cyclopentadienyl manganese tricarbonyl is methylcyclopentadienyl manganese tricarbonyl.

26. As a new composition of matter, a fuel for internal combustion engines consisting essentially of a gasoline containing from about 0.05 to 6.0 grams per gallon of

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manganese as a cyclopentadienyl manganese tricarbonyl antiknock agent and from about 0.009 to 0.1 weight percent, based on sulfur, of a sulfur-containing material selected from the class consisting of elemental sulfur, carbon disulfide and organic sulfur-containing compounds selected from the group consisting of sulfides, disulfides, polysulfides, thiophenese and mercaptan compounds, said compounds characterized by containing up to about 12 carbon atoms in the molecule and containing only sulfur, carbon and elements selected from the group consisting of hydrogen, oxygen, nitrogen, chlorine, and phosphorus.

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