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PATENTS ACT 1990 651116

PATENT REQUEST : STANDARD PATENT

I/We being the person(s) identified below as the Applicant(s), request the grant of a patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying standard complete specification.

Full application details follow:

[71/70] Applicant(s)/Nominated Person(s):

Ethyl Corporation

of

451 Florida Boulevard, Baton Rouge, Louisiana, 70801, United States of America

[54] Invention Title:

Gasoline engine fuels of enhanced properties

[72] Name(s) of actual inventor(s):

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Basic Convention Application(s) Details:

[31] Application Number	[33] Country	Code	[32] Date of Application
552090	United States of America	US	13 July 1990

DATED this FOURTH day of JULY 1991

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a member of the firm of DAVIES & COLLISON for and on behalf of the applicant(s)

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NOTICE OF ENTITLEMENT

We, Ethyl Corporation, the applicant named in the accompanying Patent Request state the following:-

The Nominated Person is entitled to the grant of the patent because the Nominated Person derives title to the invention from the inventor.

The Nominated Person is entitled to claim priority from the basic application listed on the patent request because the Nominated Person is the assignee of the applicant in respect of the basic application, and because the basic application was the first application made in a Convention country in respect of the invention.

DATED this FOURTH day of JULY 1991

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a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

(D&C ref: 1415999)

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GASOLINE ENGINE FUELS OF ENHANCED PROPERTIES

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(56) Prior Art Documents
US 4437436
US 3127351
WO 87/01384

(57) Claim

1. A gasoline having a target octane number, which comprises (i) a hydrocarbonaceous blend of base fuel blending components of the gasoline boiling range and (ii) at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number, whereby the tailpipe exhaust products resulting from use of such gasoline in a spark ignition internal combustion engine have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products resulting from use in such engine of a gasoline consisting of component (i) additionally containing an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number.

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COMPLETE SPECIFICATION

NAME OF APPLICANT(S):

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INVENTION TITLE:

Gasoline engine fuels of enhanced properties

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

This invention relates to fuels for gasoline engines and more particularly to gasoline fuels having superior environmental and performance properties.

The invention is believed to provide a most effective and efficient way of providing and using gasolines of suitable octane values while concomitantly reducing the potential for ground ozone formation, smog formation, and other greivous consequences of atmospheric pollution by reducing the maximum reactivity of exhaust products emitted by spark-ignition internal combustion engines.

Embodiments of this invention are:

(A) a gasoline having a target octane number, which comprises (i) a hydrocarbonaceous blend of base fuel blending components of the gasoline boiling range and (ii) at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, such amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number, whereby the tailpipe exhaust products resulting from use of such gasoline in a spark ignition internal combustion engine have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products resulting from use in such engine of a gasoline consisting of component (i) additionally containing an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number,

(B) a process of formulating gasoline having a target octane number, which process comprises achieving such target octane number by blending together base fuel blending components of the gasoline boiling range and at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number, whereby the tailpipe exhaust products produced by the manganese-containing formulated gasoline have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products produced by the same base fuel blending components not containing any cyclopentadienyl manganese tricarbonyl compound but containing in lieu thereof an amount of one or more aromatic gasoline

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hydrocarbons required to achieve the same target octane number.

(C) a process of operating a spark-ignition internal combustion engine which uses a gasoline fuel of suitable octane quality, which process comprises using as the gasoline fuel for said engine a formulated gasoline of suitable octane quality which comprises (i) a plurality of hydrocarbons of the gasoline boiling range and (ii) at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same octane quality, whereby the tailpipe exhaust products resulting from use of such formulated gasoline in said engine have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products resulting from use in said engine of a gasoline consisting of component (i) additionally containing an amount of one or more aromatic gasoline hydrocarbons required to achieve the same octane quality.

(D) a gasoline fuel composition having a reduced ozone-forming reactivity when used to operate a spark-ignition internal combustion engine, said composition comprising a blend of a plurality of hydrocarbons of the gasoline boiling range and a small amount of at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein which is used in lieu of an amount of one or more hydrocarbons required to achieve the same target octane number, said gasoline fuel composition being further characterized in that on combustion in said engine, the C_1-C_{10} hydrocarbons in the exhaust emitted by said engine has a maximum reactivity which is less than the maximum reactivity of the C_1-C_{10} hydrocarbons in the exhaust emitted by said engine when operated on said same plurality of hydrocarbons of the gasoline boiling range devoid of any said cyclopentadienyl manganese tricarbonyl compound.

(E) a method of reducing the maximum reactivity of tailpipe exhaust products resulting from the combustion in a spark-ignition internal combustion engine of a predominantly hydrocarbonaceous blend of base fuel blending components of the gasoline boiling range comprising saturates, olefins and aromatics, said blend having a target octane number, said method comprising:

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a) adjusting the proportions of the saturates and the aromatics of said blending components so that the resulting blend has (i) a smaller proportion of aromatics, (ii) a larger proportion of saturates and (iii) an octane number that is lower than said target octane number, and

b) including in said blend a small amount of at least one cyclopentadienyl manganese tricarbonyl compound in an amount sufficient to cause said blend have an octane number at least as high as said target octane number;

whereby said fuel produces on combustion in said engine a tailpipe emission having a reduced maximum reactivity of tailpipe exhaust products.

Other embodiments and features of this invention will become apparent from the ensuing description and appended claims.

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Figure 1 is a dimensional schematic representation of the exhaust dilution tunnel utilized in the tests described in Examples 1-4 hereinafter.

Figure 2 is a schematic representation of the vehicle emissions sampling system utilized in the tests described in Examples 1-4 hereinafter.

In each of the embodiments summarized above, the gasoline-type hydrocarbon fuels used in forming the gasoline will generally comprise saturates, olefins and aromatics; and they may also contain oxygenated fuel blending components, such as hydrocarbyl ethers. In other preferred embodiments of this invention, the fuels contain limitations on the content of aromatic gasoline hydrocarbons, inasmuch as aromatics are capable of providing exhaust product species of relatively high reactivity. Likewise, it is desirable to form or utilize in gasolines containing at most relatively small quantities of olefinic hydrocarbons (e.g., less than 10%, and more preferably less than 5% by volume), as these substances tend to produce exhaust product species of high reactivity.

At the present time the most widely used method of increasing the octane quality of pool gasoline is to utilize aromatic gasoline hydrocarbons in the base blends. Unfortunately however, certain aromatic hydrocarbons, such as benzene, are regarded as carcinogens. Moreover, and as noted above, aromatic hydrocarbons (and also olefinic hydrocarbons) tend to produce exhaust products containing relatively reactive species which are deemed to participate in the formation of ground level ozone, smog, and other forms of atmospheric pollution.

This invention overcomes this dilemma by utilizing an antiknock compound of such potency that as little as 1/32 of a gram or less per gallon manganese in the fuel gives rise to significant increases in octane quality. Thus the refiner is able to provide a gasoline having the desired octane quality while at the same time maintaining or even reducing the quantity of aromatics in the base fuel. As a consequence, the hydrocarbon tailpipe emissions resulting from use of the fuels of this invention have lower maximum reactivity than the hydrocarbon emissions of the same fuel would have if the antiknock agent were replaced by an amount of aromatic hydrocarbons necessary to achieve the same octane quality. Indeed, in at least some instances the fuels of this invention produce hydrocarbon emissions having

substantially lower total maximum reactivities than the hydrocarbon emissions from the same base fuel devoid of the cyclopentadienyl manganese tricarbonyl additive(s). This especially preferred embodiment of the invention is illustrated in Example 4 hereinafter.

Moreover, in accordance with preferred embodiments of this invention, the amount of olefinic hydrocarbons in the fuel composition can be controlled so as to be less than about 10% by volume (preferably less than 5% by volume) and, in addition, oxygenated fuel-blending components (e.g., hydrocarbyl ethers) of suitable distillation characteristics can be included in the fuel. In order to still further improve the fuel compositions from the environmental standpoint, the fuel composition should be blended from components such that the Reid vapor pressure (ASTM test method D-323) is 9.0 psi or less and most preferably 8.0 psi or less. In this way the evaporative losses of the fuel into the atmosphere during storage and fueling operations can be effectively reduced. As is well known, Reid vapor pressures are determined at 100°F (37.8°C).

The gasolines of this invention are lead-free in the sense that no organolead antiknock agent is blended into the fuel. If any trace amounts of lead are present, such amounts are due exclusively to contamination in the system in which the fuels are formed, blended, stored, transported or dispensed.

The hydrocarbonaceous gasoline base stocks that can be used in forming the gasoline blends include straight run stocks, light naphtha fractions, cracked gasoline stocks obtained from thermal or catalytic cracking, hydrocracking, or similar methods, reformate obtained by catalytic reformation or like processes, polymer gasolines formed via polymerization or olefins, alkylates obtained by addition of olefins to isobutane or other hydrocarbons by alkylation processes, isomerates formed by isomerization of lower straight chain paraffins such as a n-hexane, n-heptane, and the like, and other hydrocarbons of the gasoline boiling range formed by suitable refinery processing operations. Suitable amounts of appropriate hydrocarbons formed by other methods such as production from coal, shale or tar sands can be included, if desired. For example reformates based on liquid fuels formed by the Fischer-Tropsch process can be included in the blends. In all cases however, the resultant

gasoline must satisfy the reduced maximum reactivity tailpipe hydrocarbon emission requirements of this invention and additionally will possess the distillation characteristics typical of conventional regular, midgrade, premium, or super-premium unleaded gasolines. For example, the motor gasolines are generally within the parameters of ASTM D 4814 and typically have initial boiling points in the range of 70-115°F and final boiling points in the range of 370-440°F as measured by the standard ASTM distillation procedure (ASTM D 86). The hydrocarbon composition of gasolines according to volume percentages of saturates, olefins, and aromatics is typically determined by ASTM test procedure D 1319.

Generally, the base gasoline will be a blend of stocks obtained from several refinery processes. The final blend may also contain hydrocarbons made by other procedures such as alkylates made by the reaction of C_4 olefins and butanes using an acid catalyst such as sulfuric acid or hydrofluoric acid, and aromatics made from a reformer.

The saturated gasoline components comprise paraffins and naphthenates. These saturates are generally obtained from: (1) virgin gasoline by distillation (straight run gasoline), (2) alkylation processes (alkylates), and (3) isomerization procedures (conversion of normal paraffins to branched chain paraffins of greater octane quality). Saturated gasoline components also occur in so-called natural gasolines. In addition to the foregoing, thermally cracked stocks, catalytically cracked stocks and catalytic reformates contain some quantities of saturated components. In accordance with preferred embodiments of this invention, the base gasoline blend contains a major proportion of saturated gasoline components. Generally speaking, the higher the content of saturates consistent with producing a fuel of requisite octane quality and distillation characteristics, the better.

Olefinic gasoline components are usually formed by use of such procedures as thermal cracking, and catalytic cracking. Dehydrogenation of paraffins to olefins can supplement the gaseous olefins occurring in the refinery to produce feed material for either polymerization or alkylation processes. In order to achieve the greatest octane response to the addition of the cyclopentadienyl manganese tricarbonyl antiknock compound, the olefins, if used in the fuel blends, should be substantially

straight chain 1-olefins such as 1-heptene, 1-octene, 1-nonene, and 1-decene. Olefins of this type are known to exhibit excellent antiknock response to cyclopentadienyl manganese tricarbonyls -- see Brown and Lovell, Industrial and Engineering Chemistry, Volume 50, No. 10, October 1958, pages 1547-50.

The gasoline base stock blends with which the cyclopentadienyl manganese tricarbonyl additive is blended pursuant to this invention will generally contain 40-90 volume % of saturates, up to 30 (and preferably less than 10 and more preferably less than 5) volume % olefins, and up to 45 volume % aromatics. Preferred gasoline base stock blends for use in the practice of this invention are those containing no more than 40% by volume of aromatics, more preferably no more than 30% by volume of aromatics, still more preferably no more than 28% by volume of aromatics, and most preferably no more than 25% by volume of aromatics. Preferably, the overall fuel blend will contain no more than 1% by volume and most preferably no more than 0.8% by volume of benzene.

Particularly preferred unleaded gasolines produced and/or utilized in the practice of this invention not only meet the emission reactivity criteria of this invention, but in addition, are characterized by having (1) a maximum sulfur content of 300 ppm, (2) a maximum bromine number of 20, (3) a maximum aromatic content of 20% by volume, (4) a maximum content of benzene of 1% by volume, and (5) a minimum content of contained oxygen of 1% by weight in the form of at least one monoether or polyether, such gasoline having dissolved therein up to 1/32 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl. Gasolines of this type not containing the manganese additive are sometimes referred to as reformulated gasolines. See for example Oil & Gas Journal, April 9, 1990, pages 43-48.

From the standpoint of octane quality, the preferred gasoline base stock blends are those having an octane rating of (R + M)/2 ranging from 78-95.

Any of a variety of cyclopentadienyl manganese tricarbonyl compounds can be used in the practice of this invention. Illustrative examples of the manganese compounds which can be utilized in accordance with this invention include cyclopentadienyl manganese tricarbonyl, methyl-cyclopentadienyl manganese tricarbonyl,

dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tertbutylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, and indenyl manganese tricarbonyl, including mixtures of two or more such compounds. Generally speaking, the preferred compounds or mixtures of compounds are those which are in the liquid state of aggregation at ordinary ambient temperatures, such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, and mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl. The most preferred compound because of its commercial availability and its excellent combination of properties and effectiveness is methylcyclopentadienyl manganese tricarbonyl.

In order to satisfy the reduced emission reactivity criteria pursuant to this invention, the maximum reactivity of the C_1-C_{10} hydrocarbon species emitted from an operating engine is determined utilizing the ozone reactivity values developed by William P. L. Carter of the Air Pollution Research Center, University of California, at Riverside, California.

In the case of motor vehicles, the methodology involves operating the vehicle on a chassis dynamometer (e.g., a Clayton Model ECE-50 with a direct-drive variable-inertia flywheel system which simulates equivalent weight of vehicles from 1000 to 8875 pounds in 125-pound increments) in accordance with the Federal Test Procedure (United States Code of Federal Regulations, Title 40, Part 86, Subparts A and B, sections applicable to light-duty gasoline vehicles). As schematically depicted in Figures 1 and 2, the exhaust from the vehicle is passed into a stainless steel dilution tunnel wherein it is mixed with filtered air. Samples of regulated emissions and samples for speciation of C_1-C_{10} hydrocarbons are sampled from the

diluted exhaust by means of a constant volume sampler (CVS) and are collected in bags (e.g., bags made from Tedlar resin) in the customary fashion.

The Federal Test Procedure utilizes an urban dynamometer driving schedule which is 1372 seconds in duration. This schedule, in turn, is divided into two segments; a first segment of 505 seconds (a transient phase) and a second segment of 867 seconds (a stabilized phase). The procedure calls for a cold-start 505 segment and stabilized 867 segment, followed by a ten-minute soak then a hot-start 505 segment. In the methodology used herein, separate samples for regulated emissions and for C_1-C_{10} hydrocarbon speciation are collected during the cold-start 505 segment, the stabilized 867 segment, and the hot-start 505 segment.

If it is desired to collect and analyze exhaust samples for aldehydes and ketones, the sampling system will include an impinger collection system (note Figure 2) enabling collection of exhaust samples continuously during the desired test cycles. The air-diluted exhaust is bubbled at a rate of four liters per minute through chilled glass impingers containing an acetonitrile solution of 2,4-dinitrophenylhydrazine and perchloric acid.

When collecting aldehyde and ketone samples, the Federal Test Procedure cycle is extended to include a four-cycle procedure for sampling the aldehydes and ketones. Thus the sampling schedule when sampling for (a) regulated emissions, (b) hydrocarbon speciation, and (c) aldehydes and ketones involves collecting samples for (a) during the cold-start 505 segment, the stabilized 867 segment, and the hot-start 505 segment. Samples for (b) are also separately collected during these three segments. However, a sample for (c) is collected continuously during the cold-start 505 segment plus the stabilized 867 segment, and another sampling is started at the beginning of the hot-start 505 segment and is extended through the ensuing stabilized 867 segment. If it is only desired to sample for (a) and for (b), the impinger system and sampling procedure associated therewith are not used.

The analytical procedures used to conduct the hydrocarbon speciation are described in Example 1 hereinafter. To analyze for aldehydes and ketones, a portion of the acetonitrile solution is injected into a liquid chromatograph equipped with a UV detector. External standards of the aldehyde and ketone derivatives of 2,4-

dinitrophenylhydrazine are used to quantify the results. Detection limits for this procedure are on the order of 0.005 ppm aldehyde or ketone in dilute exhaust.

To determine the total maximum reactivity of the speciated hydrocarbons, the value in terms of mg/mile for each speciated hydrocarbon is multiplied by the reactivity constant as developed by William P. L. Carter. These constants, which represent reactivity in terms of grams of ozone/gram of speciated hydrocarbon, as estimated by Carter, are set forth in Table 1.

TABLE 1

Hydrocarbon	Reactivity, g Ozone/g Hydrocarbon
Methane	0.0102
Ethane	0.147
Propane	0.33
n-Butane	0.64
n-Pentane	0.64
n-Hexane	0.61
n-Heptane	0.48
n-Octane	0.41
n-Nonane	0.29
n-Decane	0.25
Isobutane	0.85
Lumped C4-C5 Alkanes	0.78
Branched C5 Alkanes	0.88
Isopentane	0.88
Neopentane	0.19
2-Methylpentane	0.91
3-Methylpentane	0.95
Branched C6 alkanes	0.91
2,3-Dimethylbutane	0.74
2,2-Dimethylbutane	0.41
Lumped C6+ alkanes	0.7

2,4-Dimethylpentane	1.07
3-Methylhexane	0.85
4-Methylhexane	0.85
Branched C7 alkanes	0.85
2,3-Dimethylpentane	0.96
Isooctane	0.7
4-Methylheptane	0.72
Branched C8 Alkanes	0.72
Branched C9 Alkanes	0.68
4-Ethylheptane	0.68
Branched C10 Alkanes	0.6
3 or 4-Propylheptane	0.6
Cyclopentane	1.6
Methylcyclopentane	1.7
C6 Cycloalkanes	0.84
Cyclohexane	0.84
C7 Cycloalkanes	1.1
Methylcyclohexane	1.17
Ethylcyclohexane	1.36
C8 Cycloalkanes	1.36
C9 Cycloalkanes	1.6
C10 Cycloalkanes	1.31

Ethene	5.3
Propene	6.6
1-Butene	6.1
1-Pentene	4.2
3-Methyl-1-Butene	4.2
1-Hexene	3
C6-Terminal Alkenes	3
C7-Terminal Alkenes	2.4

C8-Terminal Alkenes	1.9
C9-Terminal Alkenes	1.6
C10-Terminal Alkenes	1.32
Isobutene	4.2
2-Methyl-1-Butene	3.7
Trans-2-Butene	7.3
Cis-2-Butene	7.3
2-Methyl-2-Butene	5
C5-Internal Alkenes	6.2
2,3-Dimethyl-2-Butene	3.7
C6-Internal Alkenes	5.3
C7-Internal Alkenes	4.4
C8-Internal Alkenes	3.6
C9-Internal Alkenes	3.2
C10-Internal Alkenes	2.8
1,3-Butadiene	7.7
Isoprene	6.5
Cyclopentene	4
Cyclohexene	3.3
α-Pinene	1.9
β-Pinene	1.9

Benzene	0.28
Toluene	1.
Ethylbenzene	1.8
n-Propylbenzene	1.44
Isopropylbenzene	1.5
Sec-Butylbenzene	1.29
C10 Monoalkylbenzenes	1.28
Meta-Xylene	6
Ortho-Xylene	5.2

Para-Xylene	5.2
C9 Dialkylbenzenes	5.3
C10 Dialkylbenzenes	4.8
1,3,5-Trimethylbenzene	7.5
1,2,3-Trimethylbenzene	7.4
1,2,4-Trimethylbenzene	7.4
C10 Trialkylbenzenes	6.7
1,2,3,4-Tetrahydronaphthalene	0.73
Naphthalene	0.87
Acetylene	0.37

The practice of this invention and the advantageous results achievable by its practice are illustrated in Examples 1-4 below. These examples are not intended to limit, and should not be construed as limiting this invention.

EXAMPLE 1

Two 1988 Ford Crown Victoria 4-door sedans of essentially equal mileage (66,578 and 67,096) were operated under the same test conditions on chassis dynamometers using dynamometer settings of 4000 lbs inertia, and road load of 11.4 hp at 50 mph. For this pair of comparative tests, a commercially-available unleaded gasoline was procured and divided into two batches. Into one batch was blended methylcyclopentadienyl manganese tricarbonyl (MMT) in an amount equivalent to approximately 1/32 gram of manganese per gallon and the octane number, viz. (R + M)/2, of the resultant fuel ("MMT Fuel") was determined. Xylenes were blended into the other batch of the base gasoline in the amount necessary to match the octane number of the MMT-containing fuel. In addition n-butane was added to the latter fuel ("XY Fuel") to match the Reid vapor pressure of the MMT Fuel. Inspection data for these two test fuels and for the base gasoline are summarized in Table 2, wherein "--" represents "not measured".

Table 2 -- Inspection Data on Test Fuels

	MMT Fuel	XY Fuel	Base Fuel
Gravity, °API (D 1298)	58.8	56.9	--
Specific Gravity, 60°F	0.7436	0.7511	--
Distillation, °F (D 86)			
IBP/5	78/97	77/95	95/--
10/20	113/141	115/145	122/--
30/40	171/195	177/203	--
50/60	215/229	221/236	218/--
70/80	240/269	254/277	--
90/95	315/343	309/335	320/--
FBP	391	386	391
Recovery, Vol %	99.0	99.0	99.0
Reid Vapor Pressure, psi (D 323)	8.95	9.05	9.2
Hydrocarbon Type, Vol. % (D 1319)			
Aromatics	32.6	37.0	28.6
Olefins	2.1	3.2	4.5
Saturates	65.3	59.8	66.9
Octane			
Research (D 2699)	97.9	97.9	97.2
Motor (D 2700)	87.9	87.8	87.3
(R+M)/2	92.9	92.9	92.2

One of the vehicles was operated on the MMT Fuel whereas the other vehicle was operated on the XY Fuel. Before testing, each vehicle was operated over a 3-bag Federal Test Procedure (United States Code of Federal Regulations, Title 40, Part 86, Subparts A and B, sections applicable to light-duty gasoline vehicles) to measure regulated emissions. The vehicles were then evaluated in duplicate at two mileage accumulation points using the above-described extended version of the Federal Test Procedure in order to collect separate samples for (a) regulated

emissions, (b) hydrocarbon speciation, and (c) aldehydes and ketones. Thus the test schedule used not only accommodated the procedure as specified in the Code of Federal Regulations, but also provided a four-cycle procedure for sampling of aldehydes and ketones. Exhaust emission rates for total hydrocarbons, carbon monoxide, and oxides of nitrogen were reported in grams/mile.

The constant volume sampler (CVS) used for the evaluations was employed in conjunction with an 18-inch diameter by 16-foot long stainless steel dilution tunnel (note Figure 1) and was run at a nominal 320 scfm. This flow rate generally provided tunnel sampling zone temperatures not exceeding 110°F during the Federal Test Procedures. A cooling fan of 5000 cfm capacity was used in front of the vehicle during all test cycles. The hood was maintained fully open during all cycles and was closed during the soak periods. Exhaust sampling was conducted employing a system used in accordance with the guidelines established in the studies reported in the following papers and reports:

Urban et al, "Regulated and Unregulated Exhaust Emissions from Malfunctioning Automobiles," Paper 790696, presented at the 1979 SAE Passenger Car Meeting, Dearborn, Michigan, June 1979;

Urban et al, "Exhaust Emissions from Malfunctioning Three-way Catalyst-Equipped Automobiles." Paper 800511, presented at the 1980 SAE Congress and Exposition, Detroit, Michigan, February, 1980;

Urban, "Regulated and Unregulated Exhaust Emissions from Malfunctioning Non-Catalyst and Oxidation Catalyst Gasoline Automobiles," EPA Report 460/3-80-003, 1980; and

Smith et al, "Characterization of Emissions from Motor Vehicles Designed for Low NO_x Emissions," Final Report EPA 600/2-80-176 prepared under Contract No. 68-02-2497, July 1980.

Table 3 summarizes the hydrocarbon speciation procedures in these tests.

Table 3 -- Sampling & Analysis Methodology for Hydrocarbon Speciation

Compounds	Collection	Analysis
C_1-C_3 hydrocarbons, benzene, toluene	Bag	GC-FID
C_4 hydrocarbons including 1,3-butadiene	Bag	GC-FID
C_5-C_{10} hydrocarbons	Bag	GC with capillary column & subambient capability - FID

The analytical procedures used to conduct the hydrocarbon speciation for C_1 to C_3 plus benzene and toluene, and the C_4 (1,3-butadiene) procedure are described in detail in the following United States Environmental Protection Agency reports:

Smith et al, "Analytical Procedures Characterizing Unregulated Pollutant Emissions from Motor Vehicles," Report EPA 600/2-79-17, prepared under Contract No. 68-02-2497, February 1979; and

Smith, "Butadiene Measurement Methodology," Final Report EPA 460/3-88-005, prepared under Work Assignment B-1 of Contract No. 68-03-4044, August, 1988.

The individual analytical procedures were as follows:

C1-C3 Hydrocarbons, Benzene, and Toluene

Dilute exhaust emissions were sampled in Tedlar bags and analyzed by gas chromatography (GC) with a flame ionization detector (FID). The compounds that were analyzed included methane, ethane, ethylene, acetylene, propane, propylene, benzene, and toluene. The GC system was equipped with four separate packed columns which are used to resolve the individual compounds. A system of timers, solenoid valves, and gas sampling valves direct the flow of the sample through the

system. The carrier gas is helium. Peak areas are compared to an external calibration blend and the hydrocarbon concentrations are obtained using a Hewlett-Packard 3353 computer system. Minimum detection limits for C_1 to C_3 compounds, benzene, and toluene are 0.05. ppmC.

C4 Hydrocarbons Including 1,3-Butadiene

The procedure used provides separations and concentration data for seven C_4 compounds, namely: isobutane, butane, 1-butene, isobutene, cis-2-butene, trans-2-butene and 1,3-butadiene. Standard constant volume sampler (CVS) bag samples and evaporative emission bag samples were analyzed for the C_4 compounds using a GC equipped with an FID. The GC system utilized a Perkin-Elmer Model 3920B GC with an FID, two pneumatically-operated and electrically-controlled Seiscor valves, and an analytical column. This column is a 9 ft x 1/8-in. stainless steel column containing 80/100 Carbopack C with 0.19% picric acid. The carrier gas is helium, which flows through the column at a rate of 27 mL/min. The column temperature is maintained at 40°C for analysis. External standards in zero air are used to quantify the results. Detection limits for the procedure are on the order of 0.03 ppmC.

C5-C10 Hydrocarbons

This procedure permits the quantitative determination of more than 80 individual hydrocarbon species in automotive emissions. The GC system utilizes a Perkin-Elmer Model 3920B GC equipped with subambient capabilities, a capillary column, and an FID. The capillary column used in the system is a Perkin-Elmer F-50 Versilube, 150-ft x 0.02-in. WCOT stainless steel column. The column is initially cooled to -139°F (-95°C) for sample injection. Upon injection, the temperature is programmed at a 7°F (4°C) increase per minute to 185°F (85°C). The column temperature is held at 185°F for approximately 15 minutes to complete column flushing. A flow controller is used to maintain a 1.5 mL/min helium carrier flow rate. The 10 mL sample volume permits determination of 0.1 ppmC with the flame ionization detector.

Utilizing the maximum ozone reactivity data set forth in Table 1 above, the total maximum reactivity of the speciated hydrocarbons from each car was deter-

mined for both the 500 and the 1000 mileage accumulation points. Table 4 summarizes the total maximum reactivity data so determined.

Table 4 -Total Maximum Reactivities of Speciated Hydrocarbons

	500 Miles		1000 Miles	
Octane Enhancer	FTP-HC*	Total Max. Reactivity	FTP-HC*	Total Max. Reactivity
1/32 g Mn/gal as MMT**	475	549	550	662
Xylenes (XY)	562	794	574	933
Difference (XY minus MMT)	87	245	24	271
% Improvement with MMT	15.5	31	4	29

* Federal Test Procedure Hydrocarbons, Milligrams per Mile
** Methylcyclopentadienyl Manganese Tricarbonyl

The data in Table 4 show that in this fuel the methylcyclopentadienyl manganese tricarbonyl caused a reduction in total hydrocarbon emissions of 15.5% at 500 test miles and 4% at 1000 test miles. Of even greater importance is the fact that at both the 500 and the 1000 mileage accumulation points, the total maximum reactivity of the emitted hydrocarbons determined as described above was approximately 30% lower (31% and 29% lower) with the MMT-containing fuel than the total maximum reactivity of the emissions from the same fuel containing the added amount of xylenes needed to match the octane quality of the MMT-containing fuel.

EXAMPLE 2

The procedure of Example 1 was repeated using as the base fuel a commercially-available unleaded regular gasoline from a different domestic oil company. Table 5 summarizes the principal inspection data for the two test fuels blended therefrom -- i.e., the MMT Fuel and the XY Fuel.

Table 5 -- Inspection Data on Test Fuels

	MMT Fuel	XY Fuel
Gravity, °API (D 1298)	62.6	61.0
Specific Gravity, 60°F	0.7290	0.7351
Distillation, °F (D 86)		
IBP/5	79/98	77/92
10/20	110/129	105/125
30/40	148/171	150/180
50/60	199/231	211/240
70/80	261/296	266/292
90/95	340/370	327/353
FBP	410	405
Recovery, Vol %	99.0	99.0
Reid Vapor Pressure, psi (D 323)	10.55	10.50
Hydrocarbon Type, Vol. % (D 1319)		
Aromatics	29.8	36.4
Olefins	4.9	5.5
Saturates	65.3	58.1
Octane		
Research (D 2699)	92.6	92.6
Motor (D 2700)	82.5	82.5
(R+M)/2	87.6	87.6

The results of the comparative tests with these fuels are summarized in Table 6.

Table 6 --Total Maximum Reactivities of Speciated Hydrocarbons

	500 Miles		1000 Miles	
Octane Enhancer	FTP-HC*	Total Max. Reactivity	FTP-HC*	Total Max. Reactivity
1/32 g Mn/gal as MMT**	510	705	478	597
Xylenes (XY)	540	870	568	844
Difference (XY minus MMT)	30	165	90	247
% Improvement with MMT	5.5	19	15.8	29

* Federal Test Procedure Hydrocarbons, Milligrams per Mile
** Methylcyclopentadienyl Manganese Tricarbonyl

The data in Table 6 show that in this fuel not only did the MMT reduce the total amount of emitted hydrocarbons by 5,5 and 15.8% as compared to the XY Fuel, but even more importantly, the total maximum reactivity of the speciated exhaust hydrocarbons from the MMT Fuel was 19 and 29% lower than the total maximum reactivity of the emissions from the same base fuel (Mn-free) containing the added amount of xylenes needed to match the octane quality of the MMT-containing fuel.

EXAMPLE 3

The procedure of Example 1 was again repeated, this time using a commercially-available unleaded regular gasoline from a different domestic oil company containing 1% by weight of contained oxygen in the form of an ether blending agent (believed to be methyl tert-butyl ether). The principal inspection data for the two test fuels blended from this base gasoline -- i.e., the MMT Fuel and the XY Fuel -- are summarized in Table 7.

Table 7 -- Inspection Data on Test Fuels

	MMT Fuel	XY Fuel
Gravity, °API (D 1298)	59.3	58.7
Specific Gravity, 60°F	0.7416	0.7440
Distillation, °F (D 86)		
IBP/5	101/120	96/115
10/20	134/157	131/158
30/40	178/198	180/202
50/60	217/239	224/240
70/80	263/305	270/302
90/95	365/401	355/400
FBP	434	440
Recovery, Vol %	99.0	99.0
Reid Vapor Pressure, psi (D 323)	6.95	7.10
Hydrocarbon Type, Vol. % (D 1319)		
Aromatics	25.2	26.4
Olefins	4.2	5.0
Saturates	70.6	68.1
Octane		
Research (D 2699)	93.0	93.0
Motor (D 2700)	83.8	84.0
(R+M)/2	88.4	88.5

Table 8 summarizes the results of this pair of tests.

Table 8 --Total Maximum Reactivities of Speciated Hydrocarbons

	500 Miles		1000 Miles	
Octane Enhancer	FTP-HC*	Total Max. Reactivity	FTP-HC*	Total Max. Reactivity
1/32 g Mn/gal as MMT**	530	600	605	689
Xylenes (XY)	536	796	590	876
Difference (XY minus MMT)	6	196	(15)	187
% Improvement with MMT	1	25	(2.5)	21

* Federal Test Procedure Hydrocarbons, Milligrams per Mile
** Methylcyclopentadienyl Manganese Tricarbonyl

The data in Table 8 show that in this fuel the total maximum reactivity of the speciated exhaust hydrocarbons from the MMT Fuel was approximately 23% lower (25 and 21% lower) than the total maximum reactivity of the emissions from the same base fuel (Mn-free) containing the added amount of xylenes needed to match the octane quality of the MMT-containing fuel. Thus even though the total amount of emitted hydrocarbons was about equal for the two test fuels, the MMT fuel of this invention produced a substantially less reactive hydrocarbon exhaust and as a consequence, had a lower ground level ozone forming potential.

Overall, the vehicle operated on the MMT Fuels emitted lower levels of hydrocarbons, carbon monoxide, and oxides of nitrogen than did the vehicle operated under the same test conditions on the XY Fuels. And as set forth in detail above, the total maximum reactivities of the hydrocarbons emitted by the vehicle using the MMT Fuels was substantially lower than the total maximum reactivities of the hydrocarbons emitted by the vehicle which used the XY Fuels. It was also observed from the tests conducted as per Examples 1-3 above that the vehicle operated on the MMT Fuel generally produced lower emissions of aldehydes such as formaldehyde,

acetaldehyde, and benzaldehyde than the vehicle operated on the XY Fuels. Fuel economies were slightly lower (1-2%) for the MMT-fueled vehicle.

EXAMPLE 4

Using the procedure of Example 1, a comparison was made as between the maximum total reactivity of the speciated hydrocarbons from the MMT Fuel of Example 1 and the same base fuel with which no additional xylenes or other aromatics were added. In short, this evaluation compared the base fuel of Example 1 with the identical base fuel containing MMT at a concentration of about 1/32 gram of manganese per gallon. Table 9 presents the averaged results obtained in these runs.

Table 9 -- Total Maximum Reactivities of Speciated Hydrocarbons

Octane Enhancer	FTP-HC*	Total Max. Reactivity
1/32 g Mn/gal as MMT**	512.6	606
None (Base Fuel)	595.0	845
Difference (None minus MMT)	82.4	239
% Improvement with MMT	14	28

* Federal Test Procedure Hydrocarbons, Milligrams per Mile
** Methylcyclopentadienyl Manganese Tricarbonyl

It can be seen from the data in Table 9 that the MMT Fuel of this invention not only produced less total hydrocarbon tailpipe emissions but even more importantly, the total maximum reactivity of the speciated hydrocarbon emissions from the MMT-fuel vehicle was substantially lower (28% lower) than the speciated hydrocarbon emissions from the clear (manganese-free) base fuel. Note also from Table 2 that the octane quality of the MMT Fuel was significantly higher than that of the clear base fuel, i.e., (R+M)/2 of 92.9 v. 92.2.

The fuels of this invention can contain one or more other additives provided such other additive or combination of additives does not excessively detract from the performance -- especially the improved exhaust emission performance such as is illustrated by Examples 1-4 -- exhibited by the same base fuel containing up to 1/32 of a gram of manganese per gallon when devoid of such other additive or additives. Antioxidants, deposit-control additives (e.g., induction system cleanliness additives, carburetor detergents, and ORI-control additives), corrosion inhibitors, metal deactivators, and oxygenated blending materials such as dihydrocarbyl ethers and polyethers, typify additives commonly utilized in gasolines, and which may be used in the fuels of this invention subject to the foregoing proviso. In short, this invention contemplates the inclusion in the fuel of any ancillary additive or combination of additives which contributes an improvement to the fuel or its performance and which does not destroy or seriously impair the performance benefits made possible by this invention.

Preferred oxygenated materials that can be blended into the fuels of this invention are ethers of suitable low volatility such as methyl tert-butyl ether, ethyl tert-butyl ether, tert-amyl methyl ether, and 2,2-diethyl-1,3-propanediol. In addition, mixtures of methyl hydrocarbyl ethers formed by catalytic methoxylation of olefin components in gasoline can be effectively utilized. Processes for producing such mixtures are known and reported in the literature. See for example U. S. Pat. No. 4,746,761, and WO 8911463, and references cited therein. Also useful are fuel-soluble esters and alcohols of suitably low volatility such as tert-butyl acetate, 1-hexanol, 2-hexanol, 3-hexanol, and polyethoxyethanols. Usually such oxygenated compounds are employed in amounts sufficient to provide up to 3 to 4 weight % oxygen in the fuel, provided such usage is consistent with existing or proposed legislation. Other suitable oxygen-containing blending agents include p-cresol, 2,4-xylene, 3-methoxyphenol, 2-methylfuran, cyclopentanone, isovaleraldehyde, 2,4-pentanedione and similar oxygen-containing substances.

Preferred antioxidants for the fuels of this invention are hindered phenolic antioxidants, such as 2,6-di-tert-butyl-phenol, 2,4-dimethyl-6-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-

tert-butylphenol, and mixtures of tertiary butylated phenols predominating in 2,6-di-tert-butylphenol. In some cases aromatic amine antioxidants can prove useful either alone or in combination with a phenolic antioxidant. Antioxidants are usually employed in amounts of up to 25 pounds per thousand barrels, the amount used in any given case being dependent upon the stability (e.g., olefin content) of the gasoline.

Another type of additives preferably utilized in the fuels of this invention are ashless detergents such as polyether amines, polyalkenyl amines, alkenyl succinimides, and polyether amide amines. Such materials can be used at treat levels of 50 to 500 pounds per thousand barrels, and more usually in the range of 100 to 200 pounds per thousand barrels.

The cyclopentadienyl manganese tricarbonyl compounds as well as the other supplemental additives or blending agents can be blended with the base fuels according to well known procedures utilizing conventional mixing equipment. This invention is directed to all such fuel compositions meeting the primary requisites of this invention.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A gasoline having a target octane number, which comprises (i) a hydrocarbonaceous blend of base fuel blending components of the gasoline boiling range and (ii) at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number, whereby the tailpipe exhaust products resulting from use of such gasoline in a spark ignition internal combustion engine have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products resulting from use in such engine of a gasoline consisting of component (i) additionally containing an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number.

2. A composition as claimed in Claim 1 wherein said base fuel blending components of the gasoline boiling range of said gasoline comprise saturates, olefins, and aromatics.

3. A composition as claimed in Claim 2 wherein said base fuel blending components of the gasoline boiling range of said gasoline comprise 40-80 volume % of saturates, and up to 45 volume % aromatics, said base fuel containing less than 1% by volume of benzene.

4. A composition as claimed in Claims 1, 2 or 3 wherein said base fuel blending components of the gasoline boiling range of said gasoline contains less than 10% by volume of olefins.

5. A composition as claimed in any one of the preceding claims wherein said base fuel blending components of the gasoline boiling range of said gasoline comprise no more than 25 volume % of aromatics, said base fuel containing less than 1% by volume of benzene.

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6. A composition as claimed in any one of the preceding claims wherein said base fuel blending components of the gasoline boiling range of said gasoline include at least one oxygenated fuel blending component.

7. A composition as claimed in any one of the preceding claims wherein said cyclopentadienyl manganese tricarbonyl compound comprises methylcyclopentadienyl manganese tricarbonyl and wherein the manganese-containing gasoline has a Reid vapor pressure (ASTM test method D-323) of 8.0 psi or less.

8. A process of formulating gasoline having a target octane number, which process comprises achieving such target octane number by blending together base fuel blending components of the gasoline boiling range and at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number, whereby the tailpipe exhaust products produced by the manganese-containing formulated gasoline have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products produced by the same base fuel blending components not containing any cyclopentadienyl manganese tricarbonyl compound but containing in lieu thereof an amount of one or more aromatic gasoline hydrocarbons required to achieve the same target octane number.

9. A process of operating a spark-ignition internal combustion engine which uses a gasoline fuel of suitable octane quality, which process comprises using as the gasoline fuel for said engine a formulated gasoline of suitable octane quality which comprises (i) a plurality of hydrocarbons of the gasoline boiling range and (ii) at least one cyclopentadienyl manganese tricarbonyl compound in an amount equivalent to up to 1/32 gram of manganese per gallon, said amount of such cyclopentadienyl manganese tricarbonyl compound(s) being used in lieu of an amount of one or more aromatic gasoline hydrocarbons required to achieve the same

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octane quality, whereby the tailpipe exhaust products resulting from use of such formulated gasoline in said engine have a maximum reactivity which is less than the maximum reactivity of the tailpipe exhaust products resulting from use in said engine of a gasoline consisting of component (i) additionally containing an amount of one or more aromatic gasoline hydrocarbons required to achieve the same octane quality.

10. A gasoline fuel composition having a reduced ozone-forming reactivity when used to operate a spark-ignition internal combustion engine, said composition comprising a blend of a plurality of hydrocarbons of the gasoline boiling range and a small amount of at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein which is used in lieu of an amount of one or more hydrocarbons required to achieve the same target octane number, said gasoline fuel composition being further characterized in that on combustion in said engine, the C_1-C_{10} hydrocarbons in the exhaust emitted by said engine has a maximum reactivity which is less than the maximum reactivity of the C_1-C_{10} hydrocarbons in the exhaust emitted by said engine when operated on said same plurality of hydrocarbons of the gasoline boiling range devoid of any said cyclopentadienyl manganese tricarbonyl compound.

11. A method of reducing the maximum reactivity of tailpipe exhaust products resulting from the combustion in a spark-ignition internal combustion engine of a predominantly hydrocarbonaceous blend of base fuel blending components of the gasoline boiling range comprising saturates, olefins and aromatics, said blend having a target octane number, said method comprising:

a) adjusting the proportions of the saturates and the aromatics of said blending components so that the resulting blend has (i) a smaller proportion of aromatics, (ii) a larger proportion of saturates and (iii) an octane number that is lower than said target octane number, and

b) including in said blend a small amount of at least one cyclopentadienyl manganese tricarbonyl compound in an amount sufficient to cause said blend have an octane number at least as high as said target octane number;

whereby said fuel produces on combustion in said engine a tailpipe emission having a reduced maximum reactivity of tailpipe exhaust products.

12. A method in accordance with Claim 11 which further comprises reducing the proportion of olefins in said base fuel blending components.

13. A method in accordance with Claim 11 or Claim 12 which further comprises controlling the proportions of said base fuel blending components such that said blend contains less than 1% by volume of benzene.

14. A method in accordance with any one of Claims 11 to 13 which further comprises controlling the proportions of said base fuel blending components such that said blend contains less than 10% by volume of olefins.

15. A method in accordance with any one of Claims 11 to 14 which further comprises controlling the proportions of said base fuel blending components such that said blend contains less than 25% by volume of aromatics.

16. A method in accordance with any one of Claims 11 to 15 which further comprises including in said blend at least one oxygenated fuel blending component.

17. A method in accordance with Claim 16 wherein said at least one oxygenated fuel blending component is an alcohol or an ether.

18. A method in accordance with any one of Claims 11 to 17 which further comprises controlling the components of the blend such that said blend has a Reid vapor pressure (ASTM test method D-323) of 8.0 psi or less.

19. A method in accordance with any one of Claims 11 to 17 wherein the amount of said at least one cyclopentadienyl manganese tricarbonyl compound is equivalent to up to 1/32 gram of manganese per gallon.

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20. A method in accordance with any of Claims 11 to 19 wherein the cyclopentadienyl manganese tricarbonyl compound used is methylcyclopentadienyl manganese tricarbonyl.

21. Gasoline fuel compositions substantially as hereinbefore described with reference to the examples and/or drawings.

DATED this 12th day of May, 1994
Ethyl Corporation
By Its Patent Attorneys
DAVIES COLLISON CAVE

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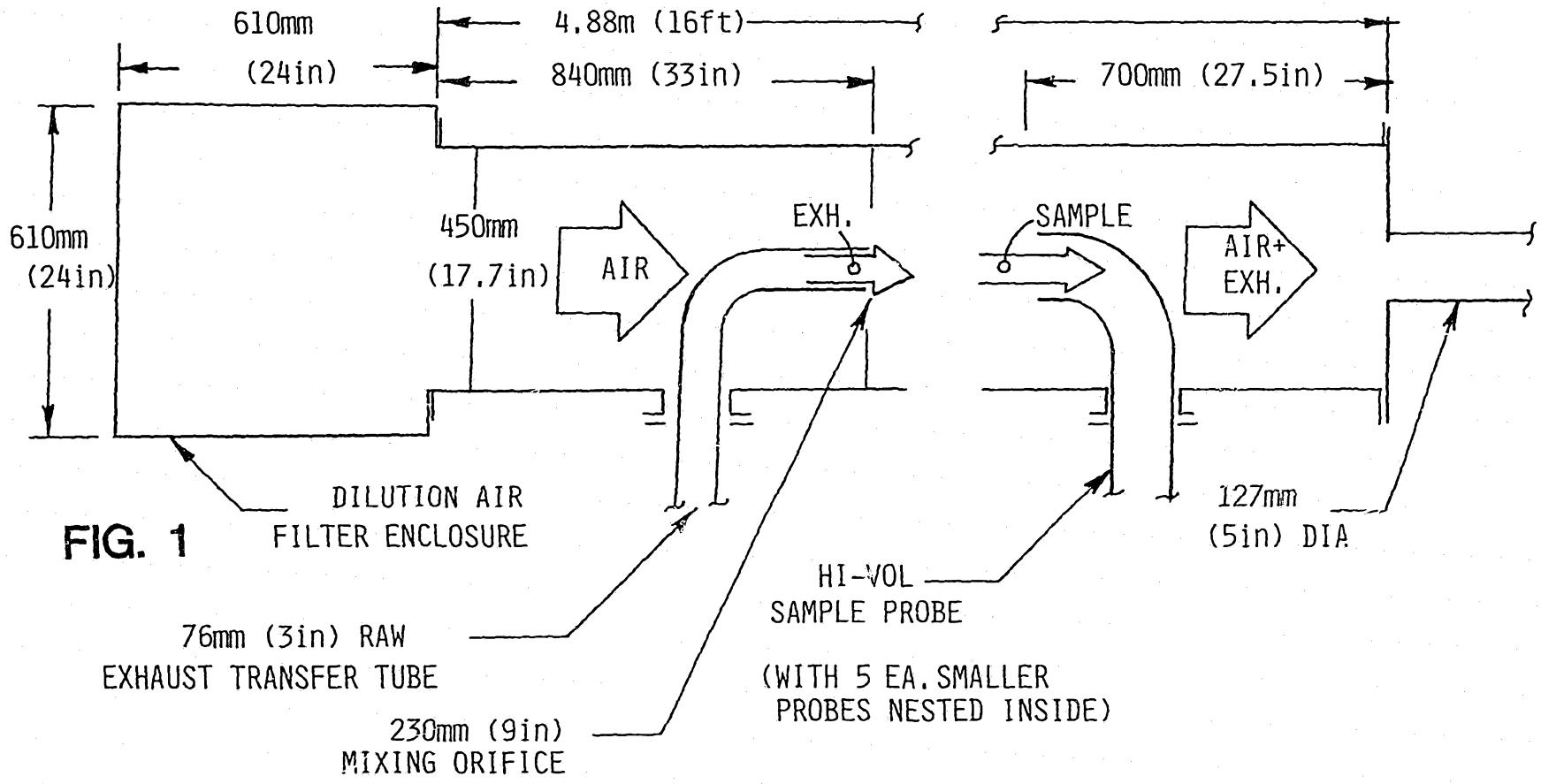
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AIR
EXH.
SAMPLE
AIR+
EXH.
DILUTION AIR
FILTER ENCLOSURE
127mm
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SAMPLE PROBE
(WITH 5 EA. SMALLER
PROBES NESTED INSIDE)
76mm (3in) RAW
EXHAUST TRANSFER TUBE
230mm (9in)
MIXING ORIFICE

FIG. 1

22 791 8016

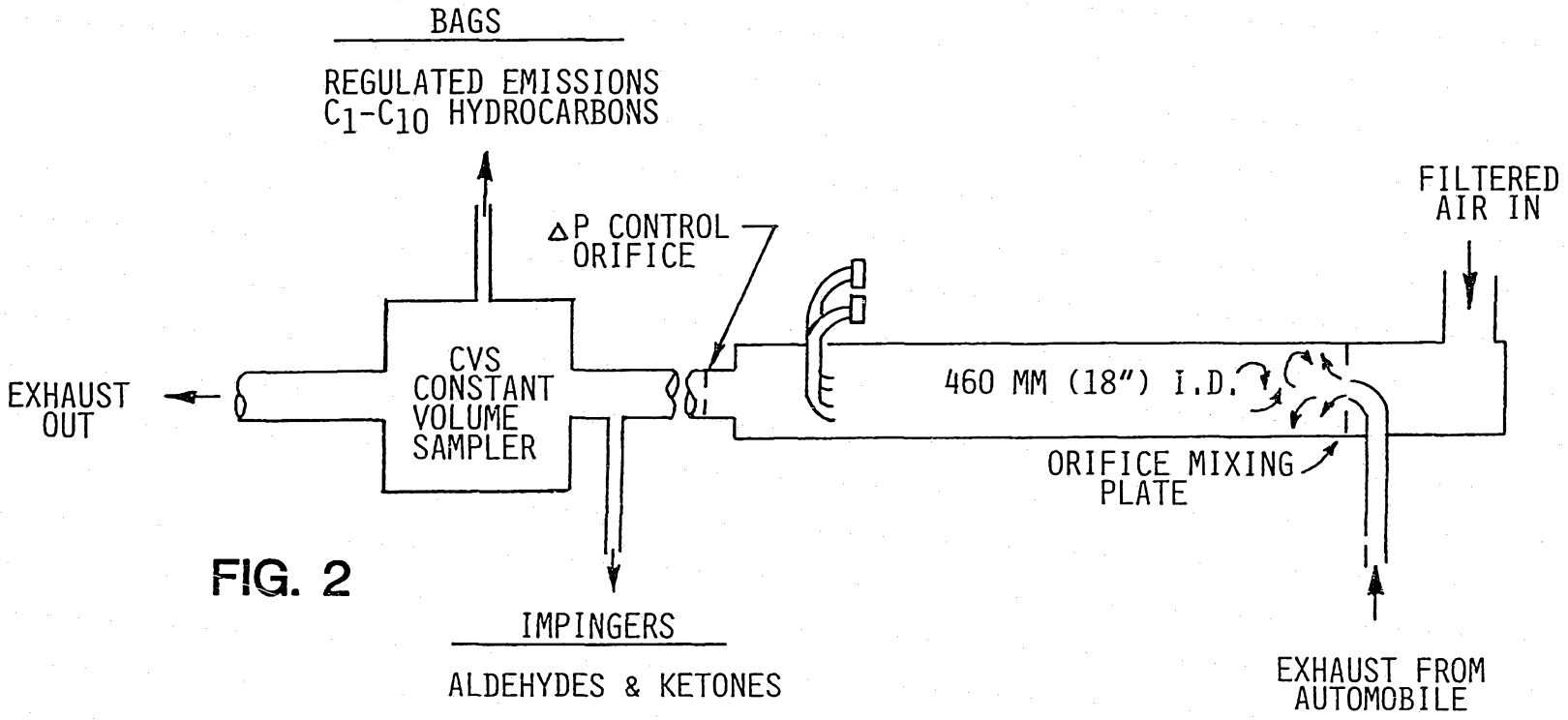

FIG. 2