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ACID ADDITIVES

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This invention relates to deposit modifiers for substantially hydrocarbon fuels. More specifically, this invention relates to substantially hydrocarbon fuels containing deposit modifiers which inhibit and/or prevent the deposit-forming tendency of hydrocarbon fuels during combustion, and/or modify the deterious effect of the formed deposits, in both leaded and unleaded fuels, particularly in gasoline, jet fuels, etc., and to the process of inhibiting and/or preventing and/or modifying the formation deposits in engines employing hydrocarbon fuels.

The smooth operation of an internal combustion engine depends on the gradual propagation of the flame toward the cylinder walls and if the fuel-air mixture is ignited at many spots at the same time, progressive combustion is interrupted. If several compressive waves are created, they subject the unburned charge to unduly high pressure and temperature so as to produce engine knock. This generally occurs if the cylinder deposits, which contain carbonaceous materials and lead compounds, retain sufficient heat to ignite the fuel-air mixture before the flame which had been originated by the spark plugs reaches all parts of the combustion chamber. Deposited lead compounds are believed to lower the temperature at which the deposits glow and ignite the fuel and it is desirable to reduce the deposits and/or neutralize the catalytic effect of such deposits in igniting the fuel. By so doing, these additives lower the octane number required to prevent knock or surface ignition.

As automobile manufacturers annually raise the compression ratio of their automobile engines in the race for higher horsepower, the need becomes greater for gasolines which burn cleanly, that is, have low deposit-forming tendencies. Engine deposits which find their origin in the fuel are primarily responsible for surface ignition phenomena such as preignition and octane requirement increase (ORI) which is the tendency of spark ignition engines in service to require higher octane fuels for proper performance. As a consequence, gasoline manufacturers have placed increasing stress on reducing the deposit-forming tendencies of their fuels and have resorted to various additives either to reduce the amount of deposits or to minimize their effects.

The deposits formed in the combustion zone, particularly on the piston head and the exhaust valves, appear to have the most immediate effects upon engine performance in that their presence requires a fuel having a higher octane rating in order not to knock, than is required by a new or clean engine. This means, in other words, that the octane value of a fuel required by an engine containing deposits in the combustion zone in order not to knock (referred to hereinafter as "octane requirement") is higher than the octane requirement of a clean engine. For example, a clean engine which requires a gasoline having an octane rating of 60 in order not to knock is said to have an octane requirement of 60. If the same engine, when dirty, i.e., with deposits in the combustion chamber, requires a gasoline having an octane rating of 75 in order not to knock, such an engine is said to have an octane requirement of 75, or an "octane requirement increase" of 15. If a clean engine starts to get dirty, the octane requirement rises with continued use. Finally there is no more octane requirement increase with continued use and apparently the engine has then become

as dirty as it is ever going to be with continued use, or if it becomes dirtier after a certain point, it does not require a gasoline of greater octane value in order not to knock.

It has been found, for example, that the weight of material deposited upon the top or head of the piston reaches a maximum in a single cylinder engine after approximately 20 hours of operation and that thereafter it decreases slightly, possibly due to a flaking action, until it levels off after about 40 hours of operation. It has also been found that the weight of the material deposited upon the exhaust valves reaches a maximum in the same engine after about 30 hours of operation and thereafter it decreases slightly and levels off after about 40 hours of operation. The fact that the weight of deposits in the combustion zone first reaches a maximum value and then levels off to a somewhat lower value while the octane requirement levels off at the maximum value is believed to disprove the formerly accepted theory that the octane requirement of an engine in proportional to the weight of deposits in the combustion chamber.

The undesirable effects of the deposits in the combustion chamber are further aggravated when tetraethyl lead is contained in the fuel because these deposits then are no longer primarily carbonaceous but contain appreciable quantities of lead. Accordingly, it has been found that the total weight of deposits formed in the combustion zone is appreciably greater when using a leaded fuel than when using a non-leaded fuel. The octane requirement increase of an engine operating on leaded fuel, however, is not in proportion to the difference in deposit weights. From this it is concluded that the octane requirement increase of an engine is determined not so much by the quantity of material deposited as by its presence and character.

It has also previously been found that the increase in octane requirement resulting from the formation of engine deposits is not attributable to a decrease in the thermal conductivity of the surfaces enclosing the combustion zone.

Since it has been found that the octane requirement increase of an engine is not determined solely by the quantity of material deposited in the combustion zone and that it is not due to a decrease in the thermal conductivity of the surfaces enclosing said zone, it is believed that it is due to a catalytic action wherein the deposits in the combustion zone act as catalysts to accelerate the oxidation of petroleum hydrocarbons. It has, therefore, been suggested that the proper approach to the problem of reducing the octane demand increase of an engine is that of adding to the fuel a substance having an anti-catalytic effect, or, in other words, the effect of suppressing or inhibiting the catalytic properties of the deposits formed, especially the troublesome lead-containing deposits.

The use of lead compounds in gasolines to increase the octane ratings thereof is extremely widespread. There are, however, several rather serious adverse effects which accompany the use of leaded gasolines. One of these effects, the deposition of various lead compounds within the combustion chambers of the engines, has been at least partially remedied by the use of halohydrocarbon scavengers such as ethylene dibromide and related compounds for example those disclosed in U.S. Patents 2,398,281, 2,490,606, 2,479,900, 2,479,902, 2,479,901, 2,479,903, etc. Another adverse effect, which has been attributed to the lead anti-knock compounds, is mis-firing due to spark plug fouling. This spark plug fouling is quite prevalent under conditions of high temperature engine operation and, particularly in the case of aircraft engines is a very serious type of trouble.

As stated above, there has been a marked trend in recent years in the automotive industry toward utilizing in-

ternal combustion engines having high compression ratios in passenger cars and trucks. It has been found that this increase in compression ratios results in increased engine efficiency whereby the motoring public is provided with both greater power availability and greater economy of operation. High compression engines almost uniformly require fuels of high octane number for most efficient operation. Of the several methods of raising the octane number of gasoline developed to date, that of utilizing an anti-knock agent, particularly of the organolead type, has been most successful. Although such anti-knock agents have been provided with corrective agents commonly known as scavengers, which effectively reduce the amount of metallic deposits in the engine by forming volatile metallic compounds which emanate from the engine in the exhaust gas stream the accumulation of engine deposits in combustion chambers and on other engine parts such as pistons, valves, and the like cannot be entirely prevented. This accumulation of deposits is particularly prevalent when the vehicles are operated under conditions of low speed and high load as encountered in metropolitan localities. As a result of the notable improvements in fuel anti-knock quality, which have been made in recent years, such deposits present but a few minor problems in low compression engines, whereas with engines of higher compression ratios two more serious problems are becoming increasingly prevalent, those of detonation and deposit-induced autoignition or wild ping. Although detonation can successfully be obviated by the utilization of organolead anti-knock agents such as tetraethyllead, it has been found that the severity of the wild ping problem often increases with the octane quality of the fuel. Hence, the automotive industry is faced with the dilemma resulting from the fact that each time the octane quality of the fuel is raised to coincide with increases in compression ratio, deposit-induced autoignition generally becomes more severe.

Ordinary detonation in the internal combustion engine has been defined as the spontaneous combustion of an appreciable portion of the charge, which results in an extremely rapid local pressure rise and produces a sharp metallic knock. The control of ordinary detonation may be effected by retarding ignition timing, by operating under part throttle conditions, by reducing the compression ratio of the engine, and by using fuels having high anti-knock qualities, that is, by using an organolead-containing fuel. Deposit-induced autoignition may be defined as the erratic ignition of the combustible charge by combustion chamber deposits resulting in uncontrolled combustion and isolated bursts of audible and inaudible manifestations of combustion, somewhat similar to knocking. Aside from the nuisance experienced by the passenger car operator, deposit-induced autoignition or wild ping often produces deleterious effects inasmuch as it is a precurser of preignition. Therefore, wild ping results in rough engine operating conditions and very often increases the wear of engine parts, piston burning and the like. In contrast to ordinary detonation, deposit-induced autoignition or wild ping cannot be satisfactorily controlled by retarding ignition timing nor by operating under part throttle conditions. Inasmuch as automotive engineers are desirous of utilizing in internal combustion engines the highest compression ratios permitted by the commercially available fuels, the reduction of compression ratios to eliminate this problem is not desirable nor feasible. Indeed, it is the consensus of opinion among the designers of internal combustion engines that engine developments have heretofore been greatly hindered by the limitations imposed by deposit-induced autoignition. It is evident, therefore, that the present requirement for fuel having high anti-knock qualities shall be greatly surpassed by future requirements. Notwithstanding attempts to attain these qualities by alternative means, it is entirely probable that the most satisfactory method for the attainment of high octane fuels shall continue to be the use of anti-knock agents, particularly of the organolead type. As a result, there is a paramount need existing for a new and improved method for altering the physical and chemical characteristics of deposits and for modifying the combustion process such that the detrimental effects of deposit-induced autoignition may be markedly suppressed or be eliminated.

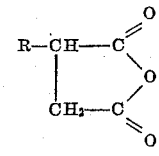
I have now found that a particular class of compounds effectively controls (by inhibiting and/or preventing and/or modifying) the deposit-forming tendencies of substantially hydrocarbon fuels, for example gasoline jet fuels and the like, with resulting advantages. The hydrocarbon fuels of this invention are characterized by low deposit-forming tendencies with the result that an engine operated therewith shows exceptionally clean intake system combustion space, valves, ring belt area, cleaner spark plugs, etc. The low deposit level in the engine, spark plugs, etc., minimizes surface ignition in all its manifestations, for example preignition, knock, wild ping, spark plug fouling, etc. The low deposit level reduces the surfaces contacted by the lubricating oil, such as piston engine's octane requirement increase, and deposits on skirts and cylinder walls, are very markedly reduced.

In addition, these compounds have an anti-catalytic effect, or, in other words, have the effect of suppressing or inhibiting the catalytic properties of the deposits found, especially the troublesome lead-containing deposits. Furthermore, these compounds are also effective corrosion inhibitors.

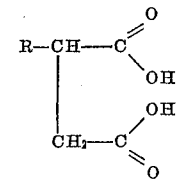
The compositions of this invention are alkenyl succinic anhydrides (ASA) or the equivalent such as alkenyl succinic acid salts thereof, and the like. Substantially any ASA or its equivalent may be employed provided it is sufficiently soluble in the fuel to be effective as a deposit modifier.

The general structural formulae of these compounds are:

Anhydride



Acid



wherein R is an alkenyl radical. The alkenyl radical can be straight-chain or branched-chain; and it can be saturated at the point of unsaturation by the addition of a substance which adds to olefinic double bonds, such as hydrogen, sulfur, bromine, chlorine, or iodine. It is obvious, of course, that there must be at least two carbon atoms in the alkenyl radical, but there is no real upper limit to the number of carbon atoms therein. However, it is preferred to use an alkenyl succinic acid anhydride reactant having between about 8 and about 18 carbon atoms per alkenyl radical.

Accordingly, when the term "alkenyl succinic acid anhydride," is used herein, it must be clearly understood that it embraces the alkenyl succinic acids as well as their anhydrides, and the derivatives thereof in which the olefinic double bond has been saturated as set forth hereinbefore. Thus, it includes the hydrogenated alkenyl group, i.e. alkyl succinic acids and anhydride. Non-limiting examples of the alkenyl succinic acid anhydride are ethenyl succinic acid anhydrides; ethenyl succinic

acid; ethyl succinic acid anhydride; propenyl succinic acid anhydride; sulfurized propenyl succinic acid anhydride; butenyl succinic acid; 2-methyl-butenyl succinic acid anhydride; 1,2-dichloropentyl succinic acid anhydride; hexenyl succinic acid anhydride; hexyl succinic acid; sulfurized 3-methylpentenyl succinic acid anhydride; 2,3-dimethyl-butenyl succinic acid anhydride; 3,3-dimethylbutenyl succinic acid; 1,2-dibromo-2-ethylbutyl succinic acid; heptenyl succinic acid anhydride; 1,2-diiodooctyl succinic acid; octenyl succinic acid anhydride; 2-methylheptenyl succinic acid anhydride; 4-ethylhexenyl succinic acid; 2-isopropylpentenyl succinic acid anhydride; nonenyl succinic acid anhydride; 2-propylhexenyl succinic acid anhydride; decenyl succinic acid; decenyl succinic acid anhydride; 5-methyl-2-isopropylhexenyl succinic acid anhydride; 1,2-dibromo-2-ethyloctenyl succinic acid anhydride; decyl succinic acid anhydride; undecenyl succinic acid anhydride; 1,2-dichloro-undecyl succinic acid; 3-ethyl-2-t-butylpentenyl succinic acid anhydride; dodecenyl succinic acid anhydride; dodecenyl succinic acid; 2-propylnonenyl succinic acid anhydride; 3-butyloctenyl succinic acid anhydride; tridecenyl succinic acid anhydride; tetradecenyl succinic acid anhydride; hexadecenyl succinic acid anhydride; sulfurized octadecenyl succinic acid; octadecyl succinic acid anhydride; 1,2-dibromo-2-methylpentadecenyl succinic acid anhydride; 8-propylpentadecyl succinic acid anhydride; eicosenyl succinic acid anhydride; 1,2-dichloro-2-methylnonadecenyl succinic acid anhydride; 2-octyl-dodecenyl succinic acid; 1,2-diiodotetracosenyl succinic acid anhydride; hexacosenyl succinic acid; hexacosenyl succinic acid anhydride; and hentriacontenyl succinic acid anhydride, as well as the corresponding acids and anhydrides of the above compounds. Salts of the above compounds in the acid state can be employed, for example, ammonium salts, amine salts, and in certain instances small amounts of inorganic ion salts although the latter is not as satisfactory as amine or ammonium salts since they tend to leave a residue on combustion.

The methods of preparing the alkenyl succinic acid anhydrides are well known to those familiar with the art. The most feasible method is by the reaction of an olefin with maleic acid anhydride. Since relatively pure olefins are difficult to obtain, and when thus obtainable, are often too expensive for commercial use, alkenyl succinic acid anhydrides are usually prepared as mixtures by reacting mixtures of olefins with maleic acid anhydride. Such mixtures, as well as relatively pure anhydrides, are utilizable herein.

In general, deposit-preventing, inhibiting and/or modifying amounts of the compounds are employed. For example, the products of this invention are effective as a deposit-control additive in concentrations between 0.001 and 2.0 weight percent of the fuel. Generally, "dirtier" fuels having a higher concentration of olefinic components require higher concentrations whereas cleaner burning premium fuels are improved with respect to deposit-forming characteristics by smaller concentrations. In general, "dirtier" gasolines require a concentration between 0.01 and 1.0 percent whereas clean-burning premium fuels only need a concentration of between 0.001 and 0.5 percent. There is no critical upper limit from a functional viewpoint but economics dictate that the concentration be less than 1 percent.

The compounds in this invention are effective in controlling deposits in hydrocarbon fuels having boiling points up to about 500° F. or higher, although benefits also result when they are added to fuels containing residual stocks of higher boiling point. The major application of the additive is in gasoline for automotive engines wherein fuel-derived engine deposits have become a particularly vexing problem. The deposit-forming properties of fuels designed for use in jets are also improved by the compounds of this invention. They find particular application in jet fuels which are used as cooling mediums prior to their consumption. The compound-containing jet fuel is an excellent heat exchange medium since it is relatively free from deposits in the cooling system and burner nozzle where deposits cannot be tolerated.

The deposit-forming properties of both regular and premium gasolines and aviation gasoline, whether leaded and of the non-leaded type, are improved by the addition of these compounds. The gasolines to which they are added can be broadly defined as a hydrocarbon fuel having a boiling point up to approximately 450° F.

Representative compounds for the above classes are incorporated, for example, in fuels used in automobile, aircraft, and jet engines. Laboratory tests are carried out employing these fuels in such systems.

The following examples of ASA's and corresponding acids are suitable in the process of this invention. The acids are prepared from hydrolysing the ASA.

TABLE I

Example	Alkenyl Group	Molecular Form
1a	Allyl	anhydride.
1b	do	acid.
2a	Octenyl (straight chain)	anhydride.
2b	do	acid.
3a	Octenyl (branched)	anhydride.
3b	do	acid.
4a	Decenyl (straight chain)	anhydride.
4b	do	acid.
5a	Tetrapropenyl	anhydride.
5b	do	acid.
6a	Triisobutenyl	anhydride.
6b	do	acid.
7a	Dodecenyl (straight chain)	anhydride.
7b	do	acid.
8a	Tetradecenyl (straight chain)	anhydride.
8b	do	acid.
9a	Heptadecenyl (straight chain)	anhydride.
9b	do	acid.
10a	Octadecenyl (straight chain)	anhydride.
10b	do	acid.
11a	Tricosenyl (straight chain)	anhydride.
11b	do	acid.
12a	Mixed C_{6-8} Alkenyl	anhydride.
12b	do	acid.
13a	Mixed C_{8-10} Alkenyl	anhydride.
13b	do	acid.
14a	Mixed C_{10-12} Alkenyl	anhydride.
14b	do	acid.
15a	Mixed C_{14-16} Alkenyl	anhydride.
15b	do	acid.
16a	Mixed C_{16-18} Alkenyl	anhydride.
16b	do	acid.

TEST I

Performance tests show that the present invention produces substantial improvement in engine cleanliness, as compared to the same fuel not containing the additive. The test procedure involves a 40 hour engine run on a dynamometer under conditions chosen to correlate, on an accelerated scale, with field performance. In this test a 216.5 cubic-inch, six-cylinder Chevrolet engine is run continuously for forty hours at a speed of 1900 r.p.m. (plus or minus 25 r.p.m.) under an engine load of 36 B.H.P. (plus or minus 1 B.H.P.) The jacket coolant inlet temperature is kept at 155° F. minimum, the jacket coolant outlet temperature is kept within two degrees of 170° F., and the crankcase oil temperature is kept within two degrees of 190° F. The air-fuel ratio is 14.5 (plus or minus 0.5) to 1. The spark advance is 35° (plus or minus 3°). The spark plug gap, ignition cam angle, valve clearance, exhaust back pressure and other similar conditions are also maintained at predetermined values. Before the test, the engine is disassembled and cleaned, and a new set of piston rings is installed. The engine is given a standard two-hour break-in before the actual test is begun.

After the test run of 40 hours, the engine is dismantled and inspected, and is rated on ten items, as follows:

(1) Piston skirt varnish rating.
(2) Cylinder wall varnish rating.
(3) Intake valve stem deposit rating.
(4) Intake valve tulip deposit rating.

(5) Intake port deposit rating.
(6) Overall engine sludge rating.
(7) Overall engine varnish rating.

On these first seven items, the rating runs between 0 for dirty to 10 for clean.

(8) Corrosion or rust rating (10 for none, 9 for light, 8 for medium, and 7 for heavy corrosion).

(9) Stuck ring rating (10, minus 0.5 demerit for each 90° of ring stuck in the groove).

(10) Tight ring rating (10, minus 0.5 demerit for each tight ring).

A perfectly clean engine will thus rate 100. A total rating of 85 is considered acceptable if the piston skirt varnish is 7.5 or better.

The gasoline employed in the tests is composed of about 50% mixed thermal naphtha having about 95°–400° F. boiling range, about 20% light straight-run naphtha having 95°–250° F. boiling range, about 25% heavy cracked (catalytic) naphtha having 270°–400° F. boiling range, and about 5% of light natural gasoline. It contains as additives about 1.75 ml. per gallon of tetraethyl-lead and an amine inhibitor in normal amounts. It analyzes 0.11% sulfur. Gum is present at about 2 to 5 mg. per 100 ml. in the ASTM test and the copper dish test shows about 16–26 mg. of gum per 100 ml. The gasoline has the following volatility specifications: 10% evaporated at 134°–150° F., 50% at 244°–250° F., and 90% at about 360° F. The approximate composition of the gasoline is:

		Percent
Paraffins and naphthalenes	About	66
Olefins	About	16
Aromatics	About	18
Sulfur	About	0.1
Phenols	About	0.4
Nitrogen	About	0.001

The alkenyl succinic anhydrides and the corresponding acids shown in the above table when tested in concentrations of 0.001–0.5 weight percent gave cleaner engines and therefore higher ratings than the control containing no additives.

An example of a high quality premium grade fuel with which similar results are obtained comprises mainly fluid catalytically cracked stock and straight run gasoline. This fuel has a 95 A.S.T.M. research octane rating, contains 2.74 ml. of TEL fluid per gallon, had an API gravity of 60 to 65 and a boiling point range between 100° and 400° F.; the base fuel is negative in the copper corrosion test and has an oxidation stability in the ASTM test of 240 minutes minimum. This fuel also contains minor amounts of conventional gasoline inhibitors, namely, approximately 6 pounds of N,N'-disecondary butyl-p-phenylenediamine, a gum inhibitor, per thousand barrels of gasoline, about 1.2 pounds of N,N'-disalicylidene-1,2-diamino-propane, a metal deactivator, per thousand barrels of gasoline, and about 1.1 pounds of lecithin, a tetraethyl lead stabilizer, per thousand barrels of gasoline.

Similar results are obtained with a high quality regular grade gasoline comprising a mixture of thermal cracked stock, fluid catalytically cracked stock and straight run gasoline. This regular base fuel has an 87.0 ASTM Research octane rating, contained 2.90 ml. of TEL per gallon, has an API gravity of 58.0 and a boiling range between 100° F. and 450° F.; the base fuel is negative in the copper corrosion test and has an oxidation stability in the ASTM test of 530 minutes minimum. The reference fuel also contains minor amounts of gasoline inhibitors, namely N,N'-disecondary butyl-p-phenylenediamine, lecithin, and N,N'-disalicylidene-1,2-diaminopropane.

These compositions are also similarly effective when tested in an aviation grade gasoline as exemplified by 115/130 grade aviation gasoline containing 4.6 ml. of tetraethyl lead.

The motor fuels employed in this invention comprise a mixture of hydrocarbons boiling in the gasoline boiling range. For instance, the gasoline employed can be a straight-run gasoline or a gasoline obtained from a conventional cracking process, or mixtures thereof. The gasoline can also include components obtained from processes other than cracking such as alkylation, isomerization, hydrogenation, polymerization, hydro-desulfurization, hydroforming, platforming or combinations thereof, as well as synthetic gasoline obtained from the Fischer-Tropsch and related processes.

Test II

SPARK PLUG FOULING

A production model 1956 Oldsmobile Super 88 engine is used to accomplish the evaluation. The engine is connected directly to a power absorption dynamometer through a conventional multiple disc coupling. The dynamometer and engine are fully instrumented to control operating conditions and to indicate data which are recorded hourly throughout the test.

Preparation of the engine for the test includes a thorough cleaning, inspection and measurement of all components. The engine is assembled according to the manufacturer's specifications. After subjecting the engine to an eight hour break-in a thirty two hour oil consumption check follows. During this check a speed of 2000 r.p.m. and 50 B.H.P. is maintained. At eight hour intervals the oil is drained and weighed. Having established oil consumption stability the cylinder compression pressures were measured to indicate valve condition. The cylinder heads are removed and all combustion chamber deposits eliminated.

The cylinder heads are assembled to the engine and preselected test spark plugs are installed for the first time. The engine starts on test schedule with an electro-mechanical intermittent controller attached to the throttle and dynamometer control which timed and actuated the throttle opening and dynamometer assistance for engine speed and load change. These changes are 2000 r.p.m. at 37.5 B.H.P. for five minutes and 450 r.p.m. at idle for one minute. Fifty of these cycles or five hours comprise one interval. At the completion of each interval a check is made for misfiring at 2400 r.p.m. at full load. If no misfiring is observed, the test continued for another interval of five hours. In the event of misfiring it is determined whether one or more spark plugs are failing. A criterion for test termination is three fouled plugs in three different cylinders. If less than three plugs fouled simultaneously the fouled plug or plugs are replaced with a new plug and the test continued until a total of three plugs fouled in three different cylinders. The reasons for replacing the fouled plugs with new plugs before continuing the test are:

A. To prevent upsetting test conditions which would affect fouling in other cylinders.

B. To assure that misfiring is caused by the plug or plugs in question.

C. To confirm that some abnormal condition in the cylinder is not causing unusually early fouling.

The foregoing procedure and conditions are observed for the first 139 hours of each test phase. At the end of 139 hours the conditions conducive to spark plug fouling are further enhanced. Consideration is carefully given to future possibility of test duplication before making any change. Beginning with the 140th hour of each test phase and continuing until phase termination, the following changes are in effect:

(1) The air fuel ratio is decreased from 12.4:1 to 11.1:1.

(2) The speed and load cycling is discontinued and changed to a constant speed of 2200 r.p.m. at 41.2 B.H.P.

(3) As a consequence of the above changes the fuel flow increases from 27.0 #s./hr. to 40.0 #s./hr.

(4) Instead of checking the spark plugs at five hour

intervals at full load, an observation with the DuMont Engine analyzer are made each hour without changing the speed or load unless plug fouling is detected.

Throughout the entire test a careful check is kept on oil consumption. At each 20 hours, as the test progressed, the engine is shut down for a crankcase oil level check. At each 60 hours the oil is changed.

The fuel treated with the additive is blended as follows: A 4000 gallon capacity storage tank is flushed with the base fuel. 1200 gallons of base fuel are pumped into the tank. A circulating pump is placed in operation with the intake at one end of the tank and the delivery at the opposite end of the required amount of additive is mixed with five gallons of the base gasoline. This mixture is slowly fed into the delivery stream of the fuel from the circulating pump. The fuel blend is recirculated for sixteen hours before start of the test.

The spark plugs selected for the test are AC–43. This spark plug is one degree colder in the heat range than the engine manufacturer recommends for this model. Twenty-four plugs are inspected and pre-tested under air pressure for firing for each test phase. From each batch of 24 plugs eight are selected which were nearly uniform in resistance at maximum pressure. All electrode gaps are adjusted to .040".

SPECIFICATIONS

Engine:

Oldsmobile 1956 Super 88 Type—	
No. of cylinders	90 degree V–8.
Valve arrangement	In head.
Bore and stroke	3⅞" x 3 7/16".
Piston displacement (cu. in.)	324.31.
Compression ratio	9.25:1.
Max. brake horsepower, at 4,400 r.p.m.	240.

Carburetor:

Rochester 4-barrel—

	Front Barrel jet sizes	Rear Barrel jet sizes	A/F Ratio
Standard Equipment	49	51	13.1:1
0–139 hours of test	55	51	12.4:1
140 hours to termination of test	59	55	11.1:1

Equipment air cleaner used.
The air-fuel ratio was determined by a Cambridge Exhaust Gas Tester.

Dynamometer:

Mid West eddy current water cooled 175 h.p. capacity. Torque reaction measured by a Fairbanks Morse beam scale.

Instrumentation:

The following temperatures are measured by means of mercury thermometers:

Jacket coolant in
Jacket coolant out
Intake air at carburetor
Motor oil in oil pan sump
Wet bulb
Dry bulb

Exhaust back pressures and intake manifold vacuum are measured by means of mercury manometers. Barometric pressure is observed on a convention mercury barometer and was corrected for temperature. Engine oil pressure is measured by a standard Bourdon-type gage.

The rate of fuel consumption is determined on a weight basis using a tip balance. A flowmeter in the supply line provides a check upon engine fuel consumption determined by weighing.

Engine speed is determined by an electronic counter.

Spark plug performance characteristics are observed by means of a multiple trace oscilloscope.

Both incipient fouling and 100% fouling of each spark plug are recorded in hours.

The base fuel used for the test operations is described as follows:

Composition—Mixture of straight run and catalytically cracked gasolines:	
Gravity, ° API	58.8
Bromine number	53
Doctor	Negative
Sulfur, percent wt.	0.017
Corrosion, cu. strip, 3 hrs. at 122° F.	None
Gum, A.S.T.M. mg.	2.8
Oxidation stability, A.S.T.M. minutes	600
Octane number:	
C.F.R.M.	87
C.F.R.R.	96
Reid vapor pressure at 100° F.	8.0
Distillation:	
IBP, ° F.	100
10%	133
20%	148
50%	202
90%	330
End point	386
Recovery	98.5
Residue	0.8
Tetraethyl lead, ml./gal.	2.92

Fuels containing the compositions of this invention in weight percent of 0.001 to 0.5%, according to this test, are superior to corresponding fuels containing no additive.

Since spark plug fouling is a function of the lead content of the gasoline, the optimum amount will vary with such content. Although weight ratios of 0.001–2% or more can be employed in gasolines containing about 3 cc. of tetraethylene lead or its equivalent/gallon of gasoline, generally 0.001–1% is usually sufficient for anti-fouling purposes. However, it should be understood that the optimum amount or the weight bases for one particular compound may not be the optimum amount for another compound. One reason for this is that the effectiveness of the compounds vary from one compound to another. Another reason is the variance of molecular weights so that one compound may be twice the molecular weight of another. However, by proper adjustment of concentrations, anti-fouling can be effected. These principles also apply to the other ratios herein stated.

Test III

These compounds in the above table are also tested in a 100 hour full scale reciprocity engine test employing Military Specification MIL–G–5572A grade 115/145 fuel in a Wright R 3350–30W compound engine operated according to the following cycle:

	Time per cycle (min.)
Idle	10
Take-off power and speed	5
Normal rated power and speed	30
Cruise	90
10% normal rated power and 93% normal rated	30
Cruise	90
Total ____min.	255

Two types of spark plugs are used in the engine: the AC–285, a platinum fine wire electrode plug and the AC–265 and 275 massive electrode plugs at the end of the test, the engine is disassembled and inspected for deposits and deleterious effects.

Fuels containing the composition of this invention in weight percent of 0.001 to 0.5%, according to this test, are superior to corresponding fuels containing no additive.

Test IV

The compounds in the above tables are also tested in a 100 hour full scale gas turbine engine test in a Pratt &

Whitney J57–P29 gas turbine engine employing Specification MIL–J–5624D Grade JP–4 fuel. The engine is operated for 100 hours and cycled in accordance with the Specification MIL–E–5009 Model qualification test. After 100 hours of operation, the engine combustion components and turbine sections are disassembled and inspected for deposits and deleterious effects.

Fuels containing the compositions of this invention in weight percent of 0.001 to 0.5%, according to this test, are superior to corresponding fuels containing no additive.

Although the present invention has been described with prefered embodiments, it is to be understood that modifications may be resorted to without departing from the spirit and scope thereof.

The invention includes various fuels such as all grades of gasolines which may contain a wide variety of additives such as antioxidants, organolead stabilizers, organic dyes, solubilizers, etc., as well as the halide scavengers generally employed such as ethylene dibromide and/or ethylene dichloride and other scavengers for example those disclosed in the patents listed above relating to such compositions. Such variations and modifications one considered to be within the purview and scope of the appended claims.

Compounds also included within the scope of the claims are those in the form of their salts. The basic constituent of these salts can be, for example, any of the monoamines, hydroxylated monoamines, polyamines, hydroxylated polyamines and other variations disclosed in my patent application serial No. 790,351, filed of even date, and assigned to the same assignee as the present application.

Having thus described my invention, what I claim as new and desire to obtain by Letters Patent is:

1. A process of preventing, inhibiting and modifying the formation of deposits in internal combustion and jet engines employing a substantially hydrocarbon fuel which comprises burning in such engines a fuel consisting of a liquid hydrocarbon having a boiling point up to about 500° F. and a minor amount in the range of approximately 0.001 to 2% by weight of the fuel, sufficient to prevent, inhibit and modify such deposits, of a member selected from the group consisting of an oil soluble alkenyl succinic acid and the anhydride thereof, having 8 to 31 carbon atoms on the alkenyl group.

2. The process of claim 1 where the alkenyl radical has 8–18 carbon atoms.

3. The process of claim 1 where the hydrocarbon fuel is gasoline.

4. The process of claim 3 where the alkenyl radical has 8–18 carbon atoms.

5. The process of claim 1 where the hydrocarbon fuel is a jet fuel.

6. The process of claim 5 where the alkenyl radical has 8–18 carbon atoms.

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