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DETERGENT AUTOMOTIVE FUEL

John P. Buckmann, Yorba Linda, Francis S. Liggett, Santa Ana, and Edward L. Wiseman, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California
No Drawing. Filed Jan. 20, 1958, Ser. No. 709,804
20 Claims. (Cl. 44—58)

This invention relates to automotive fuels suitable for use in modern high compression spark ignition engines. More particularly the invention relates to gasolines which tend to reduce deposition of objectionable gums and/or carbonaceous materials in carburetors of present day automotive engines. The invention relates further to highly stable gasolines which not only reduce or prevent carburetor deposits but also reduce or prevent the objectionable buildup of deposits normally occurring in intake manifolds, on intake valves and the like without appreciably increasing combustion chamber and exhaust valve deposits.

Modern carburetors suitable for use on present day automobiles are highly developed intricate mechanisms which operate satisfactorily only as long as ports, valves, passages and the like remain free from deposits. It is observed that with many carburetors and particularly with multibarrel carburetors, engines often begin to operate in a rough manner after 2,000–5,000 or more miles. The first indication of unsatisfactory operation is generally observed during idling of the engine. When this occurs, or soon thereafter, it is necessary to adjust the carburetor so that the engine will not die when the foot throttle is released. After a few such adjustments the only way to obtain satisfactory operation is to disassemble and clean the carburetor.

The reason for the unsatisfactory operation of engines referred to is that deposits tend to build up at critical points in the carburetor and, as the deposits increase, the ability to adjust the carburetor to compensate for the deposits becomes difficult. Apparently the most strategic point at which deposits form, i.e., the one which appears to have the greatest effect on idling is the body wall of the carburetor opposite and possibly slightly below the closed or idle position of the throttle plate. In idle position there is normally a certain clearance between the throttle plate and the wall of the carburetor. As carbonaceous deposits build up at this point the clearance becomes less and less for a given setting of the throttle plate and as the clearance is reduced the amount of air going past the throttle plate for a given amount of fuel is greatly reduced and the air-fuel mixture reaching the combustion chamber is much richer than it should be for satisfactory engine operation. It will readily be seen that carburetors in which such deposits have formed must be cleaned before they can satisfactorily perform their intended function.

These carburetor deposits may be due in part to gums present in the gasoline but it is believed that they are due primarily to crankcase vapors vented from the crankcase, exhaust vapors, dust, smoke, etc. The air cleaner usually employed on automotive engines does not appear to effectively remove these contaminants. Regardless of the theory as to the source of these deposits it is found that the described deposits occur to the greatest extent in stop-and-go city traffic driving where the chances of pulling air contaminated with these vapors into the carburetor are greatest. The relationship between carburetor deposits and crankcase vapors entering the carburetor is more fully described below.

Carburetor deposits are not the only deposits which affect engine operation. It is observed for example that under certain conditions of operation deposits form to a

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highly objectionable degree on intake valves, particularly on the fillet or stem side of the valve head, i.e., where the stem joins the head, and enters on the stem area adjacent thereto. These deposits may result from the gasoline or the lubricating oil or more likely both the fuel and the oil contribute to the deposit. The heaviest intake valve deposits have been observed in engines in which multigrade oils are employed. It is thought that the polymerized additive materials employed to give the extremely high viscosity index (V.I.) required in such oils are primarily responsible for these heavy deposits.

Although it is possible to reduce or prevent excessive carburetor deposits by the use of surface active or so-called detergent additives in gasolines, such materials generally tend to increase objectionable deposits in other portions of the induction systems as well as in the combustion chambers, etc., of the engines. Thus while the addition of small amounts of certain metal or non-metal sulfonates, etc., to gasolines has been found to effectively reduce carburetor deposits, these same additives appear to increase the deposits on intake valves and/or in combustion chambers and in some cases have been found to cause excessive deposits on exhaust valves causing improper seating and even resulting in "burning" of the valves. It is also observed that certain detergent additives have a tendency in some instances to cause corrosion of copper and brass parts in the carburetor. However, this objection can be eliminated by the use of certain combinations of additive materials as will be described hereinbelow.

It is an object of this invention to provide an automotive fuel which will reduce or prevent the formation of objectionable deposits in carburetors.

It is another object of this invention to provide an automotive fuel which prevents carburetor deposits and also prevents the formation of excessive deposits on intake valves and in the combustion chambers of automotive engines.

It is another object of this invention to provide a gasoline suitable for use in modern high compression automotive engines which is stable in storage, which prevents the formation of and/or removes carburetor deposits, prevents the formation of objectionable deposits in intake ports and on intake valves and does not contribute to combustion chamber deposits to any objectionable degree.

It is still another object of this invention to provide an additive combination suitable for adding to automotive gasolines, which may contain lead and/or gum inhibitors, which additive combination imparts to the gasoline the ability to prevent or decrease the build-up of deposits in the induction systems of automotive engines.

A more specific object of this invention is to provide gasolines suitable for use in internal combustion engines which gasolines are storage stable, prevent the build-up of carburetor deposits, reduce the tendency for the formation of deposits in other portions of the induction systems and yet do not tend to form exhaust valve deposits.

These and other objects of this invention, which will be apparent as the description thereof proceeds, are attained by adding to gasolines which are deficient in the ability to prevent objectionable carburetor deposits a long chain aliphatic amine which serves as a detergent. Although amines of this character prevent or control carburetor deposits, in order to prevent deposits at other locations in the induction system of automotive engines relatively small amounts of a particular hydrocarbon oil are also added to the gasoline. Furthermore, the addition of the amines described appears to cause some corrosion of copper and particularly brass parts present in carburetors, such as float valves, jets and the like. However, any deterioration of carburetor parts due to such

corrosion is entirely eliminated by the incorporation of a particular class of metal deactivators. A gasoline to which the long chain aliphatic amine, hydrocarbon oil, and metal deactivator are added prevents induction system deposits of substantially all types and is not corrosive to copper or brass parts in the induction system including the carburetor.

The long chain primary amines which are suitable for use are those having the formula RNH_2 , in which R is an alkyl or alkenyl radical having 12 to 22 carbon atoms. The amine to be employed may be a single amine or may consist of mixtures of such amines. A particularly effective amine is oleyl amine obtainable from Armour Chemical Division of Armour and Company under the name Armeen O or Armeen OD. Other suitable amines which are generally mixtures of aliphatic amines include Armeen T and Armeen TD, the distilled form of Armeen T which contains a mixture of 0-2% of tetradecyl amine, 24% to 30% of hexadecyl amine, 25% to 28% of octadecyl amine and 45% to 46% of octadecenyl amine. These Armeens (T and TD) are derived from tallow fatty acids. Lauryl amine is also suitable as is Armeen 12 or the distilled form Armeen 12D obtainable from the supplier indicated above. This product is about 0-2% of decylamine, 90% to 95% dodecylamine, 0-3% of tetradecylamine and 0-1% of octadecenylamine. Amines of the types indicated to be useful are well known in the art and may be prepared from fatty acids by converting the acid or mixture of acids to its ammonium soap, converting the soap to the corresponding amide by means of heat, further converting the amide to the corresponding nitrile and hydrogenating the nitrile to produce the amine. In addition to the various amines described, the mixture of amines derived from soya fatty acids also falls within the class of amines above described and is suitable for use according to this invention. It will be noted that all of the amines disclosed above as being useful are straight chain, unsubstituted, aliphatic primary amines.

Lower molecular weight amines such as those containing 10 or less carbon atoms per molecule are found not to have the desired detergency. Those amines having 16 to 18 carbon atoms per molecule and being saturated or unsaturated are particularly preferred.

The amount of amine to be added to the gasoline will be between about 0.1 pound and about 70 pounds per 1000 barrels or between about 0.00004% and about 0.02% by weight. Preferably between about 1.0 pound and about 10 pounds per 1000 barrels or between about 0.0004% and about 0.004% by weight will be employed in the gasoline. Smaller amounts of amine than those indicated do not appear to have much if any detergent effect as indicated by the build-up of carburetor deposits. On the other hand, amounts of amine larger than those indicated are not required in order to completely prevent build-up of deposits at critical points in the carburetor.

The hydrocarbon oil which may be added to the gasoline and which cooperates with the amine to prevent deposits in the induction system of automotive engines is a paraffinic oil of medium to light lubricating oil grade. Although it may be an untreated paraffinic distillate oil providing it is of low wax content it is preferably a solvent treated and dewaxed paraffinic distillate. It will have a viscosity at 100° F. of 200 to 700 SSU, a viscosity index above 70 and an A.P.I. gravity of 32 to 26.5. An ideal hydrocarbon oil to be used will have a viscosity of about 320 SSU at 100° F. and at 210° F. of about 52.2, a V.I. of about 85, a flash point of 445° F. and an A.P.I. gravity of about 28.6. Such an oil is referred to herein as 300 neutral oil and is a solvent treated and dewaxed Western paraffinic mineral oil distillate.

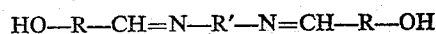
It is essential that the hydrocarbon oil employed as the second additive of our additive combination have a viscosity of between about 42 and about 78 SSU at 210° F. since lighter oils do not appear to be effective in reducing or preventing induction system deposits, e.g., in-

take valve deposits and heavier oils tend to increase combustion chamber and exhaust valve deposits. Moreover it is desirable that the oil have a flash point of at least about 400° F.

The amount of hydrocarbon oil to be used will be between about 0.02 and about 0.6% by weight of the finished composition. Preferably between about 0.03 and 0.1% by weight of hydrocarbon oil will be employed. An ideal amount is about 0.06% by weight. Although the function of the hydrocarbon oil is to reduce deposits in the induction system, particularly in the intake ports and on intake valves and the like, the manner in which this is accomplished is not known. Possibly a part of the function of the oil is that it acts as a carrier for the amine and prevents its deposition in the induction system particularly at a point where the fuel is vaporized.

As indicated hereinabove the amine has a tendency to corrode brass parts in the carburetor. Although the amount of corrosion is generally relatively small and is dependent on the amount and type of amine present, in some instances the amount is such as to be definitely objectionable. It is to be noted that the corrosion of brass parts takes place, and thus copper is dissolved in the fuel, immediately prior to the burning of the fuel. For this reason a gum problem does not generally arise, such as would be expected if the copper was present in the fuel or if the fuel was in contact with copper during periods of storage or while in the automotive fuel tank. The problem here appears to be one of protecting the carburetor parts which are generally made of brass. Such parts include the float and needle seat, idle and high speed jets and the like. Such corrosion is entirely eliminated by adding to the gasoline containing the amine a relatively small proportion of a condensation product of an o-hydroxy aromatic aldehyde with an aliphatic diamine as mentioned above and more fully described herebelow. This condensation product appears to augment the effect of the aliphatic amine in reducing carburetor deposits. This effect is not anticipated since when added to a gasoline which does not contain the amine the condensation product does not have any observable detergent effect.

Suitable metal deactivators which appear to reduce or completely prevent corrosion of brass parts in carburetors due to the presence of the long chain primary amines and which appear to cooperate with the amine in reducing carburetor deposits, are prepared by reacting an aromatic ortho-hydroxy aldehyde with an aliphatic polyamine. Preferably the aliphatic polyamine is an alkylene diamine in which the two amino groups are primary amino groups and are attached to adjacent carbon atoms. Such reaction products are well known and are prepared by condensing salicylaldehyde or alkyl or alkoxy substituted salicylaldehydes with an aliphatic polyamine in the ratio of one mol of aldehyde per primary amine group in the aliphatic polyamine. Thus 2 mols of salicylaldehyde are reacted with 1 mol of an aliphatic diamine. In this description, where the term "salicylal" is used it is meant to include the alkyl or alkoxy substituted salicylal groups as well as the unsubstituted groups. Compounds which are useful for the purposes set forth thus may be represented by the formula



where R is an aromatic group in which the OH group is ortho to the $-CH=N-$ group and R' is a bivalent aliphatic group or a group of the formula



in which R'' is a bivalent aliphatic group. Examples of such reaction products are disalicylal-ethylene diamine, disalicylal-diethylene triamine, disalicylal-triethylene-tetramine, disalicylal-propylene-diamine, disalicylal-dihexylene triamine, and the like. Thus, as indicated by the above mentioned examples the bivalent aliphatic groups are unsubstituted hydrocarbon groups containing not

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more than about 6 carbon atoms. As indicated above the aromatic group may have substituents other than the aldehyde and hydroxy groups. Substituents such as alkyl groups, alkoxy groups, and the like may be present and the resulting condensation products are suitable for the purposes mentioned herein. A particularly effective product is one prepared by condensing salicylaldehyde with 1,2-diamino-propane.

The amount of such metal deactivator to be used should be between about 0.1 pound and about 3 pounds per 1000 barrels of fuel which corresponds to between about 0.00004% and about 0.0012% by weight of the fuel composition. A particularly suitable amount when 3 to 4 pounds of amine per 1000 barrels of fuel are employed is about 1 pound per 1000 barrels. In general when larger amounts of amine are employed correspondingly larger amounts of the metal deactivator will be used and when smaller amounts of amine are used correspondingly smaller amounts of the metal deactivator will be added to the fuel.

Gasolines or automotive fuels to which the amine, amine and hydrocarbon oil, amine and metal deactivator, or amine, hydrocarbon oil and metal deactivator are to be added and in which these additives perform the functions described include substantially all grades of gasoline presently being employed in automotive and internal combustion aircraft engines. Such gasolines may be prepared from saturated hydrocarbons, e.g., straight-run stocks, alkylation products, and the like, with or without gum inhibitors, and with or without soluble lead compounds as for example tetraethyl lead, T.E.L., or ethyl fluid. The gasolines may be made wholly or partially from cracked stocks which stocks may be obtained by thermal and/or catalytic cracking methods. In such case, the gasolines will contain gum inhibitors and may or may not contain T.E.L. Generally automotive and aircraft gasolines contain both straight-run and cracked stocks with or without alkylated hydrocarbons, reformed hydrocarbons and the like. The methods of preparation of straight-run, alkylated, reformed and cracked stocks for blending in the preparation of automotive gasolines, aircraft gasolines, and the like, are well known and need not be further described. Gasoline suitable for use in present day automotive engines with which this invention is primarily concerned will generally have the characteristics shown in Table I and it is primarily to gasolines of the character indicated to which the additives of this invention are added and found to be effective.

TABLE I

Properties of typical automotive gasolines

Test	Premium Gasolines	Regular Gasolines
Gravity, °API	58-61	57-60
ASTM Gum, mg./100 ml.	Less than 1.0	1.7
Octane Rating:		
Motor method	86-89	81-83
Research method	97-100	88-92
Distillation, °F.b:		
10%	147	150
End point	425	435

^a Determined by ASTM method D-381.

^b ASTM method D-86.

The above data were obtained on two commercial gasolines of the grades indicated and are believed to be typical of commercial gasolines marketed at the present time. These gasolines contain 2-3 ml. of ethyl fluid per gallon and 5 to 15 pounds of a phenolic type gum inhibitor per 1000 barrels. It is to be pointed out that the usefulness of the additives of this invention is not limited to gasolines of the types indicated as would be understood in the art. The same additives are effective in gasolines of lower or higher volatility as well as gasolines having lower or higher knock rating, many of which gasolines are presently commercially available. Suitable gaso-

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lines may contain as much as about 5 ml. of tetraethyl lead per gallon, such amounts being used commercially in aviation gasolines. Gasolines which contain gum inhibitors may contain single materials or combinations of inhibitors. The use of gum inhibitors is well known in the art and need not be further described. It might be pointed out however that the inhibitors are generally aromatic compounds containing amino and/or hydroxyl groups and it should be mentioned further that the particular gum inhibitor or inhibitors employed does not appear to have any appreciable effect on the ability of the described additives to perform the functions described herein. When gum inhibitors are present they are employed in amounts ranging from about 5 to about 25 pounds per 1000 barrels.

The amines, hydrocarbon oil and the metal deactivator are all soluble in gasoline, and preparation of gasolines containing small amounts of these materials presents no unusual blending problems. If desired one or more of the additive materials may be dissolved in small amounts of the gasoline and the concentrate thus obtained added and mixed with the gasoline. In the case of metal deactivator compounds of this sort may be purchased from suppliers and in such case it is generally obtained as an 80% solution in an aromatic solvent such as toluene or xylene.

Various tests have been used to determine the effect of the additives of this invention in improving the characteristics of gasoline in respect to their ability to reduce or prevent carburetor deposits and deposits in other portions of the induction systems of spark ignition internal combustion engines. These tests and the results obtained with these tests are described below.

Detergency test.—A test designed to show the ability of a fuel to prevent the formation of deposits in throat or throttle section of a carburetor has been developed and used in order to determine the effectiveness of various detergent additives in preventing such deposits. In this test conditions present in the throat of a carburetor have been simulated in that gasoline, air and exhaust from an engine are pulled into a glass chamber by means of suction, entry to the chamber being through a slot 1 inch long and 0.012 inch wide located in such a position that the gasoline, air and exhaust gases impinge on and pass downward over the surface of a 1 by 2.5 inch strip of bright aluminum foil. Because of partial vacuum in the chamber partial vaporization of the liquid fuel occurs in the same manner as it does in a carburetor. In this test deposits form on the aluminum strip just as they do on the walls of a carburetor throat.

In the test the gasoline is fed by gravity at the rate of 40 ml. per minute to the slot above referred to. Vacuum is applied to the chamber to pull air and fuel downward over the test strip. Air entering the chamber is contaminated with the exhaust gases produced by a one cylinder, one horsepower gasoline engine operated with a rich fuel mixture. The exhaust from this engine is passed through three knock-out chambers so as to separate and remove all materials present in the exhaust which are liquid at ordinary temperatures.

In carrying out this test in the simulated carburetor throat, after the test strip is wet with gasoline, air contaminated with exhaust is pulled into the chamber and passed in contact with the aluminum strip. Gasoline, at the rate indicated above is permitted to flow down the aluminum strip for a period of two minutes then the supply is shut off for two minutes. This cycle is repeated 4 times, the total time of test being 16 minutes. At the end of the test the amount of deposit on the aluminum test strip is evaluated visually. The proportion of the area of the strip stained with deposits is determined and the relative thickness of the deposit is estimated by observing blackness of the deposit. A very thin coating is greyish due to the fact that the metal shows through the deposit. As the deposit becomes thicker it appears

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black. The deposits are rated on a scale of 1 to 10, where 10 represents a strip completely free of deposits and 1 represents a test strip substantially completely covered with black deposits. So that variations in conditions of operation are not reflected in test results, blank runs are made at close intervals. Thus the base gasoline to which additives being tested are added will be run at the start of a period of tests and run again at intervals to be sure that conditions of operation are maintained such that comparable results are obtained in a series of tests.

The following Table II shows the results of tests on gasolines with and without the additives of this invention. All percentages are given in percent by weight.

TABLE II
Detergency test

No.	Fuel Composition	Detergency Rating ^a
1	Base fuel ^b	2
2	Fuel No. 1 plus 0.0014% Armeen OD	9-
3	Fuel No. 2 plus 0.06% 300 neutral oil	9-
4	Fuel No. 3 plus 0.0004% disalicylal-1,2-propylene diamine.	9
5	Fuel No. 1 plus 0.0007% Armeen OD	6
6	Fuel No. 5 plus 0.03% 300 neutral oil and 0.0002% disalicylal-1,2-propylene diamine.	6
7	Fuel No. 1 plus 0.0014% Armeen TD	8+
8	Fuel No. 7 plus 0.06% 300 neutral oil and 0.0004% disalicylal-1,2-propylene diamine.	8+
9	Fuel No. 1 plus 0.002% lauryl amine.	7
10	Fuel No. 9 plus 0.06% 300 neutral oil and 0.0004% disalicylal-1,2-propylene diamine.	7+
11	Fuel No. 1 plus 0.0014% octylamine.	2+
12	Fuel No. 11 plus 0.06% 300 neutral oil and 0.0004% disalicylal-1,2-propylene diamine.	2+
13	Fuel No. 1 plus 0.0007% oleyl amine.	6
14	Fuel No. 13 plus 0.06% 300 neutral oil.	6
15	Fuel No. 14 plus 0.0004% disalicylal ethylene diamine.	6+
16	Fuel No. 14 plus 0.0004% di(2-hydroxybenzal)-triethylene tetramine.	6
17	Fuel No. 1 plus 0.0028% oleyl amine.	10-
18	Fuel No. 17 plus 0.06% 300 neutral oil and 0.001% disalicylal-1,2-propylene diamine.	10
19	Fuel No. 1 plus 0.30% 300 neutral oil.	2
20	Fuel No. 1 plus 0.0012% disalicylal-1,2-propylene diamine.	2

^a Rated on a scale of 1 to 10 where 10 represents a strip completely free of deposits and 1 a strip substantially completely covered with deposits.
^b A commercial premium gasoline of 87/88 octane rating containing straight-run and catalytically cracked hydrocarbon base stocks, 2.95 ml. of lead per gallon and 0.005% of a phenolic type gum inhibitor.

It will be seen from the data of Table II that the base fuel, i.e., the gasoline without amine, oil or metal deactivator has a very low detergency. The addition of octyl, amine (Fuels No. 11 and 12) shows substantially no increase in detergency. Thus a C₈ amine has substantially no effect on detergency. Moreover, the addition of mineral oil (Fuel No. 19) or metal deactivator (Fuel No. 20) does not improve the detergency of the base fuel.

On the other hand, the addition of fatty amines or other amines of C₁₂ and above greatly reduces deposits and thus increases detergency of the base fuel. The addition of mineral oil to fuel containing amine does not affect detergency whereas the addition of metal deactivator does seemingly improve slightly the detergency of fuel containing the amine.

Carburetor deposit test.—This is an accelerated engine test used to determine the effectiveness of gasolines to prevent buildup of deposits in carburetors.

A 1955 Oldsmobile V-8 engine is used for the test. The standard four barrel carburetor is used, however only two barrels of the carburetor are used because of low speed operation. A flexible, 1" I.D. metal tube is run from the breather pipe to the intake of the air cleaner which is an oil bath air cleaner from which the oil has been removed. Also air is pumped into the crankcase at the rate of 0.1 cu. ft. per minute. The engine is operated 15 seconds at 1500 r.p.m. and then 45 seconds at 450 r.p.m., and this cycle is repeated for 44 hours. During the higher speed the engine is operated under a 30 pound load and 11.25 brake horsepower. The coolant tempera-

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ture out is maintained at 165±5° F. and the air/fuel ratio is 12 to 13/1 throughout the test. A non-compounded SAE 20 paraffinic oil is used in the crankcase.

At the end of the 44 hour test the carburetor is rated for deposits on the curtain area below the butterfly valve and the ridge which for purposes of this description is ridge of deposit which forms as a circular deposit immediately below the butterfly valve when it is in its closed position. The rating is done on a scale of 1 to 10 where 10 represents a completely clean area and 1 represents deposits present over the entire area being rated.

Following this rating the two barrels of the carburetor are washed with a light petroleum naphtha to remove naphtha soluble materials, the deposits are then removed by scraping, dried in an oven at 105° C. to constant weight and then weighed. The total weight of deposit from both barrels is recorded as the weight of deposit in this test.

Table III gives the results of carburetor deposit tests on gasolines with and without the additives of this invention.

TABLE III
Carburetor deposit test

No.	Fuel Composition	Deposit Weight, grams	Detergency Rating ^a	
			Curtain	Ridge
1	Base fuel ^b	0.031	2.7	4.0
2	Fuel No. 1 plus 0.0014% Armeen OD, 0.06% 300 neutral oil.	0.0065	6.5	6.5
3	Fuel No. 2 plus 0.0004% disalicylal-1,2-propylene diamine.	0.0065	6.4	6.2
4	Fuel No. 1 plus 0.0014% Armeen TD.	0.008	6	5.8
5	Fuel No. 4 plus 0.06% 300 neutral oil, 0.0004% disalicylal-1,2-propylene diamine.	0.007	6	5.8
6	Fuel No. 1 plus 0.0014% lauryl amine.	0.015	5	5
7	Fuel No. 6 plus 0.06% 300 neutral oil, 0.0004% disalicylal-1,2-propylene diamine.	0.014	5	6
8	Fuel No. 1 plus 0.0028% Armeen OD.	0.0072	5	5
9	Fuel No. 8 plus 0.0004% disalicylal-1,2-propylene diamine.	0.0025	8.5	7.5
10	Fuel No. 8 plus 0.12% neutral oil, 0.0004% disalicylal-1,2-propylene diamine.	0.0039	7.5	5.5

^a Rating scale is from 1 to 10 where 10 represents a completely clean area and 1 represents deposits present over entire area being rated.
^b Same as footnote (b) Table II.

Table III shows that the addition of an amine of this invention reduces the weight of deposit in a carburetor and increases the detergency rating on both the curtain and ridge. Moreover the metal deactivator in combination with the amine appears to reduce deposits to a greater extent than the amine alone whereas the metal deactivator alone has substantially no effect on the carburetor deposits.

Other compounds referred to herein as metal deactivators and described as condensation products of ortho hydroxy aromatic aldehydes and aliphatic diamines have the same effects as those described in Table III for the metal deactivator shown there.

Road load detergency test.—This test is run in a standard six cylinder 1952 Chevrolet 216 cubic inch automobile engine with a standard carburetor and is used to determine the relative amounts of deposits on intake valves, which valves operate relatively dry, i.e., without oil flooding, using various fuels. The engine is operated for 40 hours at 2500 r.p.m. with a load of 20 brake horsepower. Cooling water is circulated through the cooling system of the engine at a rate such that with 110° F. water entering the engine, the water leaving the engine is 120° F.±5° F. The oil is maintained at a temperature of 170° F.±5° F.

Following completion of the 40-hour run the intake valves are removed, the surfaces of the valves facing the combustion chamber are scraped and/or buffed free of

deposits and the valves are then washed with naphtha to remove naphtha-soluble materials. The amounts of naphtha-insoluble deposits on the fillet and adjacent stem area is determined by weighing. This test, although it does not give absolute values, does give comparative data from which the effectiveness of various gasoline additives in preventing or reducing deposition on intake valves can be evaluated. The results are reported as naphtha-insoluble deposits per 6 valves.

In this test it is believed that the deposits are largely from the fuel rather than the crankcase oil. This conclusion is reached since the intake valves operate with a minimum of lubrication and therefore very little crankcase oil reaches the valve tulips. The data shown in the following Table IV were all obtained using an SAE 20 heavy duty crankcase oil. The only variations were in the fuel employed.

TABLE IV
Road load detergency test
PART 1

No.	Fuel Composition	Naphtha Insoluble Intake valve deposits Average, grams/valve
1	Base fuel ^a	0.250
2	Commercial Premium Gasoline A ^b	0.610

PART 2

3	Fuel No. 1 plus 0.0014% Armeen OD	0.329
4	Fuel No. 1 plus 0.0028% Armeen OD	0.786
5	Fuel No. 4 plus 0.061% 300 neutral oil	0.320
6	Fuel No. 3 plus 0.06% 300 neutral oil, 0.0004% disalicylal-1,2-propylene diamine	0.317
7	Fuel No. 3 plus 0.06% 300 neutral oil, 0.001% disalicylal-1,2-propylene diamine	0.260

^a Same as footnote (b) Table II.

^b A commercial gasoline of 97 knock rating containing lead, gum inhibitor and a detergent additive.

Part 1 of Table IV shows that whereas a premium gasoline which does not contain additives other than the conventional additives such as tetraethyl lead and gum inhibitor permits the formation of but relatively small amounts of intake valve deposits, a commercial gasoline containing detergent additives gives relatively large amounts of such deposits.

In Part 2 of the table the addition of amine is shown to permit the formation of intake valve deposits. Where a medium viscosity paraffinic hydrocarbon oil is added, or when paraffinic oil and metal deactivator is added, the amount of deposit is reduced.

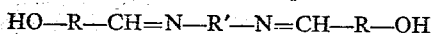
Road tests have been made in 40 automobiles for an average of about 2800 miles using premium and/or regular gasolines containing 0.004% by weight of oleyl amine and 0.24% by weight of 300 neutral oil. All of these automobiles were found to operate entirely satisfactorily during this test.

The above description and examples of our invention are illustrative of the broader aspects of this invention and are not to be taken as limiting the invention as set forth in the following claims.

We claim:

1. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range containing between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted aliphatic primary amine containing between about 12 and about 22 carbon atoms.

2. The internal combustion engine fuel according to claim 1 in which said amine is a fatty amine; said composition containing also between about 0.00004% and about 0.0012% by weight of a compound of the formula



in which R is an aromatic group in which the OH group

is ortho to the $-\text{CH}=\text{N}-$ group and R' is a group of the class consisting of bivalent aliphatic groups and $-\text{R}''-\text{NH}-\text{R}''-$ groups in which R'' is a bivalent alkyl group, all of said bivalent aliphatic groups being unsubstituted hydrocarbon groups containing not more than about 6 carbon atoms.

3. The internal combustion engine fuel according to claim 1 in which said amine is oleyl amine.

4. The internal combustion engine fuel according to claim 1 in which said amine is derived from soya fatty acids.

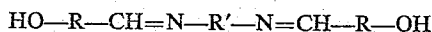
5. The internal combustion engine fuel according to claim 1 in which said amine is derived from tallow fatty acids.

6. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range containing between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted, aliphatic primary amine containing between about 12 and about 22 carbon atoms, and between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.

7. The internal combustion engine fuel according to claim 6 in which said amine is a fatty amine.

8. The internal combustion engine fuel according to claim 6 in which said amine is oleyl amine.

9. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range containing between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted, aliphatic primary amine containing between about 12 and about 22 carbon atoms, and between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.; and between about 0.00004% and about 0.0012% by weight of a compound of the formula



in which R is an aromatic group in which the OH group is ortho to the $-\text{CH}=\text{N}-$ group and R' is a group of the class consisting of bivalent aliphatic groups and $-\text{R}''-\text{NH}-\text{R}''-$ groups in which R'' is a bivalent alkyl group, all of said bivalent aliphatic groups being unsubstituted hydrocarbon groups containing not more than about 6 carbon atoms.

10. The internal combustion engine fuel according to claim 9 in which said amine is a fatty amine.

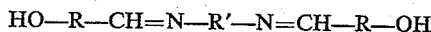
11. The internal combustion engine fuel according to claim 9 in which said amine is oleyl amine.

12. The internal combustion engine fuel according to claim 9 in which said amine is derived from soya fatty acids.

13. The internal combustion engine fuel according to claim 9 in which said amine is derived from tallow fatty acids.

14. The internal combustion engine fuel according to claim 9 in which said last named compound is disalicylal-1,2-propylene diamine.

15. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range containing between about 0.0004% and about 0.004% by weight of straight chain, unsubstituted aliphatic primary amine containing between about 12 and about 22 carbon atoms; between about 0.03% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.; and between about 0.00004% and about 0.0012% by weight of a compound of the formula



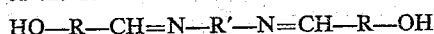
in which R is an aromatic group in which the OH group is ortho to the $-\text{CH}=\text{N}-$ group and R' is a group of the class consisting of bivalent aliphatic groups and

—R''—NH—R''— groups in which R'' is a bivalent alkyl group, all of said bivalent aliphatic groups being unsubstituted hydrocarbon groups containing not more than about 6 carbon atoms.

16. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range and containing up to 5 ml. of tetraethyl lead per gallon; between about 5 and about 25 pounds per 1000 barrels of a phenolic type gum inhibitor; between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted, aliphatic primary amine containing between about 12 and about 22 carbon atoms.

17. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range and containing up to 5 ml. of tetraethyl lead per gallon; between about 5 and about 25 pounds per 1000 barrels of a phenolic type gum inhibitor; between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted, aliphatic primary amine containing between about 12 and about 22 carbon atoms; and between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.

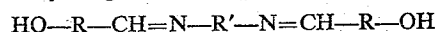
18. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range and containing up to 5 ml. of tetraethyl lead per gallon; between about 5 and about 25 pounds per 1000 barrels of a phenolic type gum inhibitor; between about 0.00004% and about 0.02% by weight of straight chain, unsubstituted, aliphatic primary amine containing between about 12 and about 22 carbon atoms; and between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.; and between about 0.00004% and about 0.0012% by weight of a compound of the formula



in which R is an aromatic group in which the OH group is ortho to the —CH=N— group and R' is a group of the class consisting of bivalent aliphatic groups and —R''—NH—R''— groups in which R'' is a bivalent alkyl group, all of said bivalent aliphatic groups being unsubstituted hydrocarbon groups containing not more than about 6 carbon atoms.

19. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range and containing up to 5 ml. of tetraethyl lead per gallon; between about 5 and about 25 pounds per 1000 barrels of

a phenolic type gum inhibitor; between about 0.0004% and about 0.004% by weight of a primary fatty amine containing between about 12 and about 18 carbon atoms; between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. between 42 and 78 SSU and a flash point of at least 400° F.; and between about 0.00004% and about 0.0012% by weight of a compound of the formula



in which R is an aromatic group in which the OH group is ortho to the —CH=N— group and R' is a bivalent aliphatic group, all of said bivalent aliphatic groups being unsubstituted hydrocarbon groups containing not more than about 6 carbon atoms.

20. An internal combustion engine fuel consisting essentially of hydrocarbons in the gasoline boiling range and containing up to 5 ml. of tetraethyl lead per gallon; between about 5 and about 25 pounds per 1000 barrels of a phenolic type gum inhibitor; between about 0.0004% and about 0.004% by weight of oleyl amine; between about 0.02% and about 0.6% by weight of a paraffinic hydrocarbon oil having a viscosity at 210° F. of between 42 and 78 SSU and a flash point of at least 400° F.; and between about 0.00004% and 0.0012% by weight of disalicylal-1,2-propylene diamine.

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