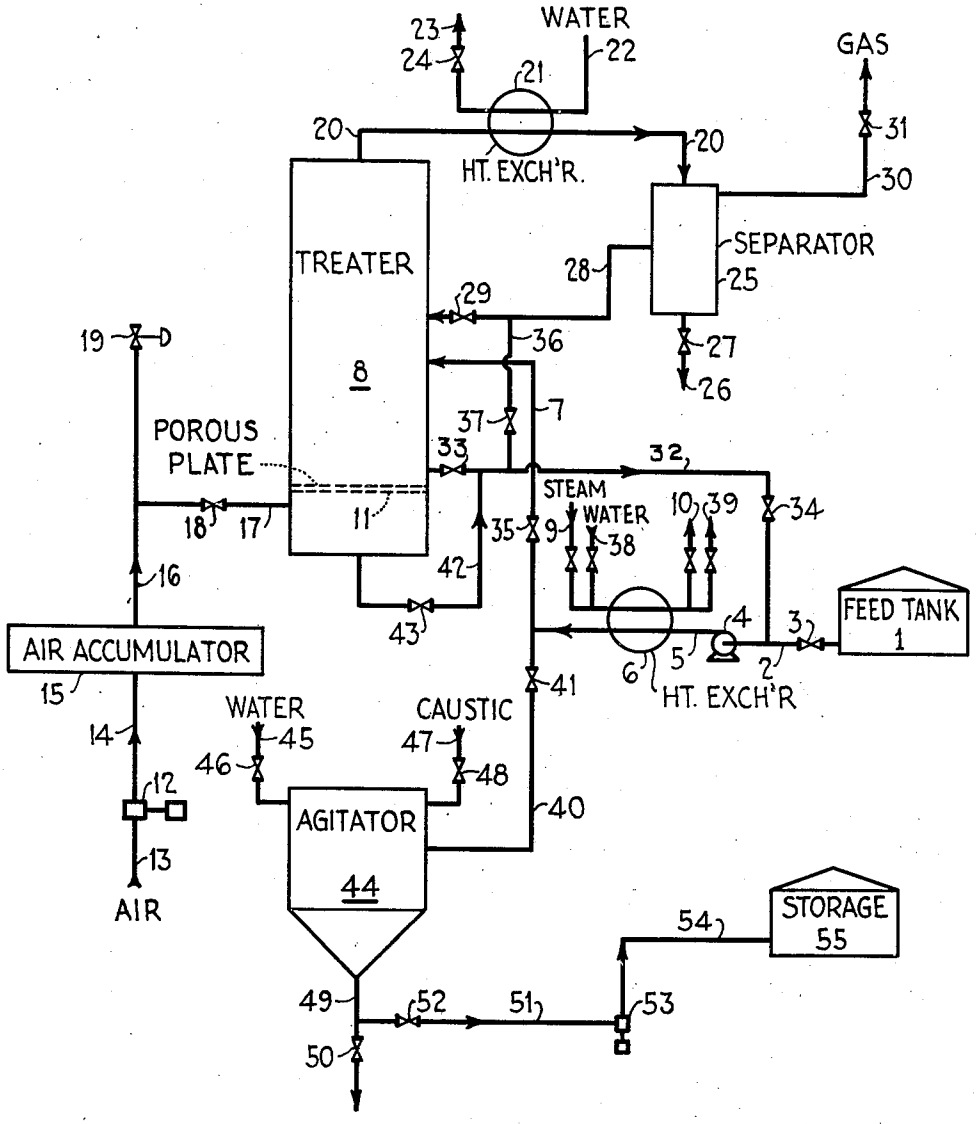
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PROCESS OF PREPARING IMPROVED INJECTION ENGINE FUELS

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INVENTORS
THOMAS H. SCHULTZ
IRVING E. LEVINE
HOMER B. WELLMAN

BY _____
ATTORNEY

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PROCESS OF PREPARING AN IMPROVED INJECTION ENGINE FUEL

Thomas H. Schultz, Richmond, and Irving E. Levine and Homer B. Wellman, Berkeley, Calif., assignors to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

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This invention relates to fuels for internal combustion engines of the Diesel type, in which a liquid fuel is injected into a combustion chamber and ignited by compression, and it has particularly to do with the modification of ordinary hydrocarbon fuels of the Diesel and more volatile than Diesel types in such a manner as to enhance their combustion characteristics for Diesel motor purposes.

In the attainment of minimum engine knocking, the time interval between the instant of liquid fuel injection and the instant of ignition, referred to as the "delay period," should be as brief as possible. Generally, this delay period is known to be affected by the type or character of the hydrocarbons composing the fuel; also, it may be shortened by the addition to the fuel of various more or less pure chemical "accelerators" or "primers," and certain organic nitrates, nitrites and peroxides are known to be effective for this purpose. Such ignition accelerators or primers are mechanically admixed with or dissolved in the fuel hydrocarbons, generally in amounts between 0.1% and 5–10% by weight of the fuel hydrocarbons. These substances are often costly and sometimes hazardous to prepare and handle; their uniform and permanent incorporation in the fuel is occasionally uncertain and, in some cases, the beneficial ignition effects are attended by adverse effects of other sorts.

In the present invention, fuels of high ignition quality, as measured by decrease in delay period and by ease of cold motor starting, are prepared by derivation from the petroleum hydrocarbons which themselves compose the usual whole Diesel fuels or may be slightly more volatile than the usual whole Diesel fuel, or fractions thereof. This derivation, in its simplest terms, is through a carefully controlled partial oxidation of a kerosene distillate or Diesel fuel hydrocarbon distillate or portion thereof, under definitely ascertained circumstances, followed by a supplementary treatment designed to stabilize the composition which is produced and to free it from components adverse in their effects upon Diesel engine operation, upon deterioration in storage, upon physical homogeneity and the like. As prepared, the fuels of the invention are low in cost, of consistently high ignition quality, sufficiently permanent and stable in storage, and generally without adverse qualities from the standpoint of marketability.

In their barest outline, the processes of the invention provide for the preliminary selection or treatment of a petroleum fuel of kerosene distillate or ordinary Diesel fuel distillate characteristics, or a portion of such a fuel, by such means as will produce a set of hydrocarbons capable upon oxidation with air or an oxygen-carrying gas of attaining an "oxygen factor" of higher than about 5 and preferably of higher than 50 or 100; treating the said selected or preliminarily prepared set of hydrocarbons with air, oxygen or an oxygen-carrying gas under such conditions as will allow it to attain an oxygen factor of 5 or more, generally without concomitant increase in neutralization number of more than about 15 and often of not more than about 8 or 10; arresting the said oxidizing treatment before the oxygen factor of the oil has decreased to below about 5; and removing acidic oxidation products that have been ascertained to be detrimental for the purposes of the invention. This partially oxidized oil may be employed as an injection engine fuel, in and of itself, or it may be blended with one or more ordinary hydrocarbon fractions of the same or different boiling point characteristics to produce a fuel of the desired high ignition quality. The partially oxidized oils contain chemically combined oxygen in significant quantities, dependent upon the oxygen factors obtained; for example, an oil of high oxygen factor may contain 2.0% or more of chemically combined oxygen.

The processes and the compositions of the invention may best be described by reference to a number of specific examples.

Example I.—A Midway (California) crude gas oil distillate fraction having the following characteristics:

Gravity	°API	28.9
Pour point	°F Below	—70
Viscosity, SSU at 100° F		38.5
Cetane No		35
Initial boiling point	°F	358
50% boiling point	°F	515
End boiling point	°F	718
U. O. P. characterization factor		11.27
Cold engine starting temperature	°F	66

was treated at ordinary temperature with 1.0 pound of 98% H_2SO_4 per gallon. The sludge was settled and removed and the treated oil was washed with water, neutralized with caustic soda solution and again washed with water to remove acidic products and soaps of sulfonic acids, in the usual manner. The treating yield was 93 volume per cent, and the treated gas oil then had the following characteristics:

Gravity	°API	30.3
Pour point	°F Below	—70
Viscosity, SSU at 100° F		38.2
Cetane No		36.5
U. O. P. characterization factor		11.32
Cold engine starting temperature	°F	62.5

This preliminary treated oil was heated to 290–300° F. and transferred to a vertical cylindrical vessel or "still" of chrome-nickel steel equipped with a horizontal porous plate partition near the

bottom (Filtros plates grade R, manufactured by Filtros Inc., East Rochester, New York) and provided with heating or cooling coils and with a vapor condenser. A concentrated solution of calcium naphthenate in oil was added, in an amount such that the final proportion of the salt was 1.0% by weight; also 2% by volume of "seed stock" (completely prepared fuel of the invention, from an earlier preparation) was added.

The oil was maintained at 290–300° F. and air, finely dispersed by passage through the interstices of the porous plate partitions, was passed therethrough for 1½ hours at the rate of 2 volumes of air per minute per volume of oil. During the first part of the reaction heat was supplied through the coils, to compensate for the cooling caused by evaporation; during the latter part of the reaction less heat was needed and cooling is indeed sometimes required, as the reaction is exothermic; in any case, such oil as evaporated was liquefied in a stainless steel condenser, condensed water was trapped out, and the condensed oil was returned directly to the main reaction mixture. After 1½ hours of blowing under these conditions, the oil had an oxygen factor of 425, a neutralization number of 4.9 and a saponification number of 19.3. The blown oil was then cooled rapidly to 100° F. by passage through a heat exchanger, air passage being continued in the main vessel until it was empty of oil.

The blown oil was washed at atmospheric temperature with water, in which the calcium salts or soaps of moderately strong organic acids became suspended or dissolved and were hence removed from the oil. Such organic acids as were present in the oil were then removed by scrubbing with 5% caustic soda solution, added in an amount not over 10% in excess of that required. Finally, the oil was washed with water and brightened in a rock brightener in the usual manner. The characteristics of the finished oil were as follows:

Gravity	°API	27.7
Pour point	°F	−55
Viscosity, SSU at 100° F		42.0
Cetane No		62
Oxygen factor		338
Saponification No		12.5
Soap No		0.01
Neutralization No		0.27
Cold engine starting temperature	°F	45

Example II.—A Kettleman Hills (California) crudelight gas oil distillate having the following characteristics:

Gravity	°API	36.9
Pour point	°F	−45
Viscosity, SSU at 100° F		34
Cetane No		42
Initial boiling point	°F	360
50% boiling point	°F	450
End boiling point	°F	538
U. O. P. characterization factor		11.52
Cold engine starting temperature	°F	58

was pumped through a heat exchanger and heated to 300° F., then transferred to the vessel or still referred to, equipped with a porous plate partition near the bottom. A concentrated solution of calcium naphthenate in the same distillate was added in an amount such that the final proportion of the salt was 0.5% by weight. "Seed stock" (previously air-blown Kettleman distillate) was added to the extent of 2% by volume of the charge.

The temperature of the charge was maintained at 290–300° F. and air, finely dispersed by the porous plate partition, was blown through it for 1½ hours at two volumes air per minute per volume of oil. The blown oil was then rapidly cooled to 100° F. by passage through a heat exchanger, continuing the air passage in the reaction vessel until the same was empty of oil. This oil had, at this stage, an oxygen factor of 522, a neutralization number of 5.9 and a saponification number of 20.0.

The oil was washed with water to remove calcium salts of organic acids (by partial solution and suspension in the water) and free acids were then removed by scrubbing with 5% caustic soda solution in very small excess only, after which the scrubbed oil was again water-washed until the soap number was below 0.005, and finally brightened.

The characteristics of the oil thus prepared were as follows:

Gravity	°API	34.7
Pour point	°F	−45
Viscosity, SSU at 100° F		34.6
Cetane No		75
Oxygen factor		432
Soap No		0.001
Saponification No		12.6
Neutralization No		0.2
Cold engine starting temperature	°F	36

Example III.—A clean Kettleman Hills (California) medium gas oil distillate having the following characteristics:

Gravity	°API	33.4
Pour point	°F	+5
Viscosity, SSU at 100° F		39.0
Cetane No		51.5
Initial boiling point	°F	500
50% boiling point	°F	542
End boiling point	°F	628
U. O. P. characterization factor		11.66
Cold engine starting temperature	°F	52

was blended with the finished oil prepared as described in Example II, the proportions of the blend being 86 volume per cent of the clean Kettleman Hills medium distillate and 14 volume per cent of the 75 cetane number oil prepared in accordance with Example II. The characteristics of the blended oil were as follows:

Gravity	°API	34.1
Pour point	°F	0
Viscosity, SSU at 100° F		38.5
Cetane No		61
Oxygen factor		62
Cold engine starting temperature	°F	46

Definitions.—For the purposes of this invention, the following characteristics have the following meanings or derivations:

The cetane number determinations given herein are determined by a procedure known as the Standard Oil Company of California delay method, employing a Fairbanks Morse Diesel engine, in which the ignition delay with combustion occurring at top dead center is utilized as the test criterion and in which the operating variable is the injection advance, equivalent to the ignition delay when firing is made to occur at top dead center. In brief, this procedure is characterized as follows: The fuel to be tested is introduced into the engine and the injection is then advanced or retarded until firing occurs at top center; the ignition delay is read and recorded. The

procedure is then repeated for a series of cetane-alphamethylnaphthalene blends which produce greater and lesser ignition delays than the fuel under test. A plot is made of the ignition delays of the cetane-alphamethylnaphthalene blends in terms of the percentage of cetane in the blends. The ignition delay of the fuel under test is placed on this plot and its corresponding cetane number is determined. The method may be employed on service engines capable of sufficient control of all operating variables, other than Fairbanks Morse; as described, the method yields results which correlate well with service performance.

The cold engine starting temperatures given herein are determined by a procedure known as the Standard Oil Company of California cold starting method, in which the lowest ambient temperature at which the engine will start in just 5 seconds is measured under service conditions. In brief, this procedure is characterized as follows: The fuel to be tested is introduced into the fuel system of a single cylinder, 1400 R. P. M. precombustion chamber, 4½" x 5½" bore and stock, 16 to 1 compression ratio, full scale Caterpillar Diesel engine with injection advance set at 23° BTC and an injection pressure of 1500 lbs./sq. in.; suitable refrigerating equipment is provided to cool the intake air and cylinder jacket to the required low temperatures. Jacket and intake air temperatures are established with the engine stopped, and the engine is then cranked at 280 R. P. M. (the normal cranking speed for this engine) until firing occurs; the time interval between first injection of the fuel and the first firing explosion is measured and recorded as the cranking time. The procedure is repeated with the jacket and intake air temperature either raised or lowered as required to result in starting with just 5 seconds of cranking. This final temperature, an ambient starting temperature of the fuel, is that referred to as cold engine starting temperature; this temperature may be correlated with the cetane number of the fuel. These determinations are representative of field performance.

For the purposes of this invention, the "oxygen factor" of an oil is determined as follows: A 2 to 10 ml. sample of the oil, at approximately 68° F., is accurately pipetted into a 250 ml. glass-stoppered flask. 20 ml. of a mixture consisting of 60 volumes per cent of C. P. glacial acetic acid and 40 volume per cent of chloroform are added to the oil, followed by 2.0 ml. of a saturated aqueous solution of potassium iodide. The mixture is shaken vigorously for three minutes and then diluted with about 50 ml. of distilled water. The liberated iodine is titrated with 0.1 normal standardized sodium thiosulfate solution, adding starch indicator just before the end point is reached. Considerable shaking is necessary near the end of the titration. Oxygen factor=(titer in ml.×normality of thiosulfate×1120)/(volume of sample in ml.).

For the purposes of the invention, the "soap number" of an oil is determined as follows: A 5 to 100 ml. sample of the oil is pipetted into a 250 ml. Squibb funnel, and 10 ml. of saturated aqueous sodium chloride sclution, approximately 3 grams of solid sodium chloride and 2 drops of methyl orange indicator are added. The mixture is titrated with standardized dilute hydrochloric acid solution (1 ml. equivalent to 1.0 mg. of KOH) until a pink color persists in the aqueous layer after 30 seconds of vigorous shaking and then settling: A light neutral petroleum thinner may be added to hasten settling, if necessary. A blank titration is made, omitting the oil sample, and the titer subtracted from the titer obtained with the oil, to obtain the corrected titer. Soap number=(corrected titer×concentration of HCl in equivalent mg. of KOH per ml.)/(weight of oil sample), the weight of oil sample being derived from volume and specific gravity of the oil tested.

Saponification numbers are determined in accordance with A. S. T. M. D94–38T, Method A. Neutralization numbers are determined in accordance with A. S. T. M. D188–27T, Method B, modified by titration at room temperature, by the use of alcoholic hydroxide and by the use of ethyl ether in place of alcohol. U. O. P. characterization factors are discussed in Watson, Nelson and Murphy, Industrial and Engineering Chemistry, volume 27, pages 1460–1464 (1935).

The paragraphs below discuss the critical nature of several of the variables which operate to provide the maximum benefits in the practice of the invention.

The precise character of the oil contemplated for use has been found to be of considerable consequence in providing a set of hydrocarbons capable of attaining high oxygen factors upon being subjected to the action of oxygen or an oxygen-containing gas such as air, under the circumstances disclosed for the practice of the invention. In general, the factors which have been found of greatest significance in this choice or preliminary preparation of an oil are: relative freedom from large proportions of aromatic ring structures among the hydrocarbons themselves; relative freedom from asphaltic or resinous materials; and relative volatility of the set of hydrocarbons as a whole.

Oils containing high proportions of aromatic rings are less easily capable of attaining high oxygen factors than are oils of high "paraffinicity," although the treatment of oils of high aromatic content with relatively strong sulfuric acid or an equivalent chemical reagent or their extraction with liquid solvents such as liquid sulfur dioxide, phenol, aniline, furfural, nitrobenzene and the like, in removing aromatic components or reducing their concentration, suffices to improve their amenability to treatment in accordance with the invention. These effects are illustrated in Table I.

Table I

	Oil	Pretreatment	Maximum oxygen factor
1	380°–720° F. Kettleman gas oil.	None	123
2	360°–720° F. Midway gas oil.	do	0
3	360°–720° F. Midway gas oil.	0.5 lb. 98% H_2SO_4/gal	266
4	360°–720° F. Midway gas oil.	2.0 lbs. 98% H_2SO_4/gal	450
5	360°–720° F. Midway gas oil.	Extraction with 100% SO_2.	272

The Kettleman gas oil referred to in Table I was a clean distillate, containing substantially no asphaltic or resinous matter; it is understood to contain some 7–16% of aromatic rings and some 60–70% of paraffins, including side chains. The Midway gas oil referred to was likewise a clean distillate, understood to contain some 15–23% of aromatic rings and some 50% of paraffins, in-

cluding side chains. The preliminary treatments carried out on the Midway gas oil as above illustrated increase the paraffinicity of the oil as a whole, to varying degrees, and make the desired type of oxidation more readily possible.

Further, the presence of small amounts of resinous or asphaltic substances appears to prevent the attainment of high oxygen factors in the oils, and the removal of such substances, which may be present by reason of spray or mist entrainment in the original fractionation of the oil, may be effected by a subsequent re-fractionation to eliminate heavy ends, by treatment with clay or analogous adsorbent agents, or by sulfuric acid or solvent extracting treatments. These effects are illustrated in Table II.

Table II

	Oil	Pretreatment	Maximum oxygen factor
1	380°–720° F. Kettleman gas oil.	None	0
2	380°–720° F. Kettleman gas oil.	0.5 lb. 98% H_2SO_4/gal	378
3	380°–720° F. Kettleman gas oil.	2.0 lbs. 98% H_2SO_4/gal	520
4	380°–720° F. Kettleman gas oil.	Extraction with 100% SO_2	342
5	380°–720° F. Kettleman gas oil.	Percolation thru fuller's earth.	206
6	490°–680° F. Kettleman gas oil.	(Re-fractionation)	148

The Kettleman gas oil referred to in Table II was the overhead from an imperfect fractionating column and contained small amounts of asphaltic or resinous matter introduced by spray entrainment, as was evidenced by the color of the distillate itself: Refractionation of the distillate or treatment with clay were each sufficient to remove this material and allow the desirable reactions to progress. As in the case of the Midway distillate referred to in Table I, reagent or solvent treatment effected marked improvement even in the relatively highly paraffinic 380°–720° F. Kettleman distillate referred to in Table II, since the quantities of such agents as are there exemplified do more than remove merely asphaltic substances and go far toward aromatic ring removal.

Finally, the boiling point range or relative volatility of the oils affects their relative oxidizability to produce the types of compounds whose presence is measured in terms of oxygen factor and found desirable for the purposes of the invention. Thus the oils capable of attaining highest oxygen factors are those of ordinary kerosene boiling point range of average volatility, and maximum attainable oxygen factor decreases as average volatility decreases. This effect is illustrated in Table III.

Table III

A. S. T. M. boiling points			Maximum oxygen factor
Initial	50%	End	
341	394	491	780
374	477	542	494
402	530	611	282
490	561	680	148

The oil stocks referred to in Table III were all clean distillates from the same crude Kettleman Hills, California, source. In general, as average volatility decreases, preliminary treatment with acid, clay or a selective solvent or analogous treating agent is more effective to increase the maximum attainable oxygen factor than it is to increase the maximum oxygen factor attainable on relatively volatile oils.

The oil stocks exemplified in Tables I, II and III, above were treated with air at 300° F. under similar conditions: 6 volumes air per minute per volume oil; 1.0% calcium naphthenate and 2.5% of "seed stock" as accelerators, and the operations were continued for a sufficient time to reach the maximum oxygen factors attainable under these conditions. Sulfuric acid of higher or lower strength, for example 93% H_2SO_4 to 20% SO_3, in variable amounts, and solvents similar in their action to liquid SO_2, likewise in higher or lower amounts than those shown, are suitable for use in the pre-treatments described, when such treatment is indicated as desirable for the removal of the originally contained deleterious hydrocarbon components. Similar relations between oxidizability of the desired type and relative freedom from aromatic rings, asphaltic or resinous matter, and average volatility may be ascertained for operations on oil stocks of different origin than those particularly exemplified above.

Residual petroleum stocks cannot be employed as initial materials in the processes of the invention unless they have been preliminarily subjected to a refining treatment equivalent to an overhead vaporization, for the substantially complete removal of the high boiling asphaltic, resinous and highly reactive hydrocarbons ordinarily contained in petroleum residua. In general, it may be said that when the processes are to be carried out on sets of hydrocarbons of petroleum origin and of the usual straight run or cracked distillate types, relatively free of asphaltic and resinous material, U. O. P. characterization factors should be 11.15 or above; if the U. O. P. characterization factor of such a set of hydrocarbons, prepared in any usual manner from a petroleum source material, is below 11.15, a preliminary treatment of the nature of those indicated will be found necessary. Original or treated distillates of 11.30 or higher U. O. P. characterization factors may be employed to greater advantage in the oxidizing steps than those with lower factors, and the highest benefits of the process may be obtained from stocks with factors of 11.50 and higher. From this it will be seen that the oxidizing processes of the invention are not ordinarily to be used, in the absence of preliminary treatment, on petroleum stocks which are themselves unusable as Diesel engine fuels: on the contrary, insofar as ordinary petroleum fractions are concerned, the processes of the invention contemplate an improvement in stocks already of recognized utility as medium- or high-speed compression ignition engine fuels.

In still further illustration of the wide variety of hydrocarbon stocks which may be beneficially treated in accordance with the invention:

A side cut gas oil stream from a thermal cracking unit, of light Diesel oil volatility, had a delay method cetane number of 31 and a U. O. P characterization factor of 11.12; upon extraction with 200% of liquid SO_2, the raffinate had a cetane number of 54 and a U. O. P. characterization factor of 11.74. This raffinate was blown

for 1¼ hours with 4 volumes of air per minute per volume of oil, at 300° F., in the presence of 1% of calcium naphthenate, and the treated oil washed with water and dilute caustic soda solution in the manner described. The finished treated oil had an oxygen factor of 280 and a delay method cetane number of 80.

In the oxidizing step in the process of the invention, temperatures between 200° and 400° F. may be employed, but operations between 250° and 350° F. are more suitable; the preferred range is between 275° and 325° F. and 290–310° F. is optimum, almost irrespective of charging stock and of the character of the preliminary treatment. At temperatures below 275° F., the reactions which progress are of highly beneficial character and products of high oxygen factor are obtained; the rate of reaction, however, is considerably lower than it is within the preferred range. Temperatures above about 310° F. are usually avoided as the temperature coefficient for the rate of secondary and deleterious reactions, in which the substances giving rise to high oxygen factors are destroyed, is greater than the temperature coefficient for the rate of formation of these primary and desirable substances. The table below will illustrate the effect of temperature on the results obtained in treating the Kettleman gas oil referred to in Table II, above, preliminarily prepared with a 0.5 lb. 98% H_2SO_4/gal. treatment, at an air rate of 4 volumes air per minute per volume oil, in the presence of 1.0% calcium naphthenate and 2.5% of seed stock as catalysts and accelerators, with air passage through a porous plate in finely dispersed condition.

Time, hours	275° F.		300° F.		325° F.	
	O_2 factor	Neut. No.	O_2 factor	Neut. No.	O_2 factor	Neut. No.
0.5					150	2.0
0.75					225	4.5
1.0	10		150		200	
1.25				2.8	170	7.5
1.5	30		335		150	
1.75			378	4.5		
2.0	70		370			
2.25				7.7		
2.5	130		280			
3.0	210					
4.0	325					
4.25		3.9				
4.75	440	4.4				
5.0	375					
5.5	350	5.6				

It will be observed that the oxygen factor reaches a maximum and thereafter decreases rapidly, whatever the temperature of treatment. It is accordingly desirable to continue the treatment with air or an oxygen-carrying gas, at a high temperature, for a time not materially longer than is sufficient to give an oil of the maximum oxygen factor attainable under the circumstances of the treatment. It will likewise be observed that secondary or side-reaction products increase rapidly as this maximum oxygen factor is approached and passed; some of these acidic side-reaction products are undesirable and must be removed from the oil, for the purposes of the invention, and the continuation of the treatment is accordingly undesirable for this reason as well. It is obvious that the treatment with air or an oxygen-containing gas may be terminated at any suitable time prior to the attainment of the maximum oxygen factor, with highly desirable results.

Generally, the maximum oxygen factor attainable in an oil, when subjected to the conditions here described, will be reached and passed before the neutralization number of the oil reaches 15; it may therefore be said that ordinarily the processes of the invention do not contemplate the continuance of exposure of an oil to an oxygen-carrying gas, under reactive conditions, beyond a neutralization number rise of 15 and generally not beyond a neutralization number rise of 12; indeed, a rise in neutralization number beyond 10 and sometimes beyond 8 will often indicate that the maximum oxygen factor has been passed, to the detriment of the invention in its best aspects. In actual operations, the course of the reaction may best be observed by the periodic removal of small samples of the oil undergoing oxidation and by carrying out rapid oxygen factor determinations thereon.

Moreover, the oil should not be allowed to remain at or appreciably near an oxidizing temperature for any considerable period of time, subsequent to the attainment of the desired oxygen factor and, particularly, such holding at a reactive temperature should not be allowed in the absence of free oxygen passage. For example, if an oil of desirable and high oxygen factor is held, after air-blowing, at a temperature such as 300° F. in the absence of continuing air passage, the oxygen factor decreases rapidly and, in a period as long as two hours, approaches zero. This is to say that the secondary reactions, to which reference has been made, continue at the expense of the primary and desirable products: the value of the oil is accordingly much impaired for the purposes of the invention. It is thus important to cool the oil to a temperature below that at which this reaction is rapid, namely, to a temperature below 250° F. and preferably as low as 150° F., promptly after the desired oxygen factor has been reached.

During the air or oxygen treatment itself, the maximum oxygen factor attainable in an oil increases with air rate, other conditions remaining constant, up to the point at which bubble size increases excessively. Likewise, when the air rate (expressed in volume of air per minute per volume of oil) remains constant, the maximum oxygen factor attainable increases with the height of the liquid column, within ordinary practicable limits.

Suitable apparatus in which to effect the contact between liquid oil and oxygen-containing gas is, as described, a vertical cylindrical vessel or still equipped with Filtros or similar porous plate partitions near the bottom, up through which the gas may be disseminated in small bubbles. The porosity of the plates should be high for maximum gas utilization, and beneficial results will be obtained with decreasing pore size, down to the point at which excessive pressure drop occurs through the plates. In this type of apparatus, a liquid column of quiescent oil 4 feet in height, above the plates, and an air rate of two volumes air per minute per volume of oil has been found satisfactory; such height and air rate are dependent, however, upon pore size and upon the extent to which the oxygen factor of the oil is desired to be carried, in the manner referred to above. In the construction of this and the condensing and water-trapping apparatus, such metals as copper, brass, bronze and lead should be avoided; chrome-nickel steel is satisfactory, as is glass-lined material. In the desired

rapid cooling of the oil, subsequent to the reaction, the gas should be allowed to continue its passage through the oil until cooling is actually effected, lest the formation of secondary reaction products deplete unnecessarily the quantity of desirable primary products present.

In one mode of operation, the invention may be carried out as exemplified in the flow diagram of the appended figure.

In the figure, 1 represents a feed tank from which initial hydrocarbons, adapted for the preparation of the improved injection engine fuels of the invention, are fed to the treating system. The initial oils pass through the line 2, controlled by the valve 3, through the pump 4 and line 5 into and through the heat exchanger 6 and line 7 to a treating vessel 8. In passing through the heat exchanger 6, the oil is raised to an appropriate temperature by the passage of steam or another heating fluid through lines 9 and 10. The vessel 8 is equipped with a porous plate 11, of suitable characteristics as described. Air or an appropriate oxygen-containing gas is forced by the compressor 12, taking suction through the line 13, through line 14 into air storage vessel 15 and thence through lines 16 and 17, the latter controlled at valve 18, into vessel 8 below the porous plate 11; the line 16 carries a pressure control and release valve 19. In the vessel 8, controlled aeration of the oil takes place as described; oxygen-denuded air or other gas, carrying some water, volatile hydrocarbons and such partial oxidation products as are volatile under the conditions of the treatment, leave the vessel through the line 20, pass through the condenser 21, cooled by water entering at 22 and leaving at 23 by control of the valve 24 in appropriate quantities. Condensed water, hydrocarbons and partial oxidation products volatile under the circumstances of the treatment in the vessel 8 enter the collecting drum 25, where stratification takes place; water is withdrawn through the line 26, controlled by the valve 27; hydrocarbons and contained oil-soluble materials are returned to the vessel 8 through the line 28 by control of the valve 29; uncondensible gases leave the system through the line 30, controlled by the valve 31. In the initiation of the reaction and in order that proper oil temperature may be maintained in the vessel 8, circulation of liquid oil may be maintained through the line 32, controlled by the valves 33 and 34, into the line 2 and through pump 4, line 5 and heater 6 and returned to the vessel 8 through the line 7 under control of the valve 35; such circulation may take place during the progress of the treatment itself, if desired, and oily condensate may appropriately be passed into such circulatory system through lines 28 and 36 into line 32, valve 29 being closed and valve 37 open. When the oil in vessel 8 has been treated to the degree desired, as measured by the oxygen factor and neutralization number of samples withdrawn at suitable intervals, the heat exchanger 6 is converted to a cooler by ceasing the passage of steam therethrough through the lines 9 and 10 and the passage of water through the lines 38 and 39; the oil from the treating vessel is cooled by circulation through line 32, controlled by valves 33 and 34, into line 2 and through pump 4, line 5 and the cooler 6, through line 7, controlled by valve 35, into the vessel 8; during such cooling of the treated oil, the entry of air to the vessel 8, through the porous plate 11, is continued until the body of oil has reached a temperature below which deleterious side-reactions no longer take place. The treating system is emptied through lines 32, 2, 5 and 40, valves 33 and 41 being open and valve 35 closed; oil which has found its way below the porous plate 11 in the treater 8 may be removed through line 42 controlled by valve 43, thus finding its way into line 32. The oil in line 40 is passed to agitator 44, where it is washed with water brought in through line 45 and valve 46, and with dilute aqueous alkaline hydroxide solution brought in through the line 47 and valve 48; in the agitator 44, the aqueous washing materials are provided contact with the treated oil by appropriate spray or other suitable means. Spent aqueous wash materials are withdrawn through line 49 and valve 50. The finished oils of the invention are withdrawn from the agitator 44 through line 51, controlled by the valve 52, by the pump assembly 53 and passed by line 54 to the storage tank 55. Such a system may be operated batch or continuously, with appropriate controls, as desired.

Moreover, it is important that substantially all strongly acidic substances and salts or soaps of organic acids be removed from the treated oil prior to its employment as a fuel in Diesel engines or prior to its blending with unoxidized distillates, both to assure the stability of the finished oil and to prevent gumming and fouling of the injection nozzles and combustion chambers of the motors and, in addition, to finally stop all reactions of a secondary nature. This removal may be accomplished as exemplified above, in Examples I and II, by washing with a dilute alkali metal hydroxide solution and then with water. In removing acidic bodies subsequent to cooling after the primary oxidation step, there should be used no more than a slight excess of alkali metal hydroxide solution, and the alkaline solution is itself preferably dilute. A 2° to 10° Bé. caustic soda solution has been found suitable. When using 7° Bé. caustic soda solution, if as much as 4 times the necessary alkaline solution is employed, on the basis of the acid or neutralization number as determined, the oxygen factor of the oil will be found to be lowered remarkably, for example by as much as 170 in a high oxygen factor product; if only 10% excess caustic soda is used in acid removal, the oxygen factor may be lowered by 7–23%. In general, considerable care is justified in this step of the process, in order that oils of high oxygen factor may be retained in stable, effective form for the purposes of the invention.

As oxidation catalysts in the oxygen-reactive stages in the process of the invention, oil-soluble calcium and sodium salts are preferred, and these or equivalent alkali or alkaline earth salts of naphthenic acids, either natural or synthetic, are eminently suitable. These catalysts are most useful in proportions of about 0.25–1.0% by weight of the oil undergoing oxidation, but slightly lower and somewhat higher concentrations may be employed if desirable, for example, amounts between 0.10% and 2.5% by weight. In some cases, notably those in which clean, relatively low boiling point stocks are treated, for example a refined kerosene or lamp oil, no catalyst is required to cause the attainment of high oxygen factors. The calcium and sodium salts of the organic acids formed in the course of the oxidizing reaction itself, recoverable in the caustic soda washing step which follows the cooling of the treated oil, are themselves effective as catalysts in the oxidizing stage of the

process. In general, the use of large amounts of catalysts leads to the formation of acidic or resinous reaction products at the expense of substances measurable in terms of oxygen factor, and the quantity of catalyst should accordingly be held as low as is consistent with the oxygen factor desired to be attained. In addition, a small amount of an oxidized oil, prepared in a previous operation, taken prior or preferably subsequent to washing and neutralizing, will act to accelerate oxidation of the character here desired; the utility of such material is referred to herein under the designation "seed stock." This seed stock, while not essential, has been found in many cases to shorten the time necessary to initiate the reaction, without affecting the nature of the reaction itself. Salts or soaps of the heavier metals such as copper, iron, manganese, cobalt and the like, often employed to catalyze oxidation reactions of types other than that of this invention, are here of little or no value, as their presence leads to the formation of acidic bodies at a rate higher than can be tolerated in the necessary segregation of substances of high oxygen factor; it accordingly appears that different oxidation mechanisms may predominate when the heavy metal type catalysts are employed.

Subsequent to the removal of relatively strongly acidic reaction products, the partially oxidized oils themselves may be used as injection engine fuels, but in many cases it will be found advantageous for economic or other reasons to blend such oils with unoxidized oils to produce fuels of certain desired characteristics: see Example III above. In order to bring the proportion of the partially oxidized oil component in such blends to a minimum and to avoid a preliminary treatment prior to the oxidizing process, a paraffinic distillate of kerosene or more volatile characteristics may suitably be used as charging stock: see Table III and Example III above. In these blending operations, whether the partially oxidizing component is relatively more or less or equally volatile, the desired viscosity, gravity, boiling range and ignition quality may be realized by suitable choice of initial materials. It is advantageous, for example, to partially oxidize a high pour point paraffinic distillate, containing or preliminarily treated to contain but few aromatic rings, and to blend such an oil, properly washed to low acid and soap numbers, with a low pour point, less paraffinic stock of the same boiling range.

For the best preservation of the benefits of the invention, the stock to be blended with the partially oxidized oil should be clean and relatively free from asphaltic and resinous bodies, especially if the stock is of low paraffinicity, as small amounts of such reactive materials destroy the substances measurable in terms of oxygen factor. Generally, clean petroleum distillates of 11.15 and higher U. O. P. characterization factor should be used in blending, but in many cases improved stability in storage will be obtained by subjecting the unoxidized component of the blend to a light acid, clay or solvent refining treatment, in the manner disclosed in connection with the preparation of the partially oxidized component.

From 10 to 35% of the partially oxidized component will generally be a sufficient proportion in such blends, but from 5 to 60% may often be used, and proportions higher and lower are occasionally desirable.

The common physical properties of such blends, as the gravity, flash point and the like, may be predicted from the properties of the individual components, but the cetane numbers will be found to be higher than the values predicted in the usual manner, especially for blends in which the proportions of the partially oxidized component are low.

In this specification, repeated reference is made to cetane numbers and oxygen factors of oils. Close correlations may be worked out between oxygen factor and cetane number rise, for comparative or control purposes. For example, the relation

$$\text{Cetane No. rise} = 1.58\sqrt{\text{Oxygen factor of fuel}}$$

has been found to hold, in general, for the rather paraffinic stock referred to herein as of Kettleman Hills, California origin, whether the whole fuel was treated or, on the other hand, a fraction was treated and the finished treated fraction was blended with an untreated but clean fraction of the same or of different boiling range. The above relation may be modified somewhat with stocks of different origin, and such modifications may be worked out as desired.

The Diesel fuels prepared in the manner described are substantially stable in storage in ordinary fuel containers under all ordinary circumstances, without deterioration in ignition quality; also, the fuels are not corrosive to ordinary cast iron, black iron, mild or high carbon steel, chrome-nickel steel, Monel, bronze, brass, copper, tin or aluminum containers or parts. Nozzle and combustion chamber depositions are in general no greater than from the base stocks employed in their preparation, and in many cases less.

As used in this specification and in the appended claims, the term "injection engine fuel" refers to distillate fractions only, but it includes hydrocarbon distillate fractions of kerosene or illuminating oil boiling range and fractions of such fractions, as well as the somewhat less volatile distillates in more usual present use in internal combustion engines of the medium- and high-speed Diesel type; the term accordingly includes hydrocarbon fractions whose A. S. T. M. 50% boiling points at atmospheric pressure are within the range 325° F. to 650° F. As thus used herein, this term includes fractions of relatively narrow boiling point range (so-called "short cuts" or "heart cuts") as well as fractions of wider boiling point range (so-called "long cuts").

While various specific embodiments of the invention have been illustrated and described above it is obvious that many modifications and adaptations may be made without departing therefrom, and all such changes as are included within the scope of the appended claims are embraced thereby.

We claim:

1. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 5 but insufficient to in-

crease the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 5, and removing acidic reaction products from the produced oil without reducing the oxygen factor thereof to below about 5.

2. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 5 but insufficient to increase the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 5, removing acidic reaction products and washing the substantially acid-free oil with water without reducing the oxygen factor thereof to below about 5.

3. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 5 but insufficient to increase the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 5, and removing acidic reaction products from the produced oil without reducing the oxygen factor thereof to below about 5.

4. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F in the presence of an oil-soluble oxidation catalyst for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 50, and substantially completely removing soaps and corrosive acidic reaction products from the produced oil without reducing the oxygen factor thereof to below about 35.

5. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. in the presence of an oil-soluble oxidation catalyst for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 50, and reducing the soap number and the neutralization number of the produced oil to below 0.05 and 0.25, respectively, by washing with dilute aqueous alkaline solution and with water, in the order named, without reducing the oxygen factor of the produced oil to below about 35.

6. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 400° F. in the presence of an oil-soluble oxidation catalyst for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, arresting the said treatment before the oxygen factor of the produced oil decreases to below about 50, substantially completely removing soaps and corrosive acidic reaction products without reducing the oxygen factor of the produced oil to below about 35, and blending the said substantially soap-free and acid-free oil with from 2/5 to 20 times its volume of a clean petroleum hydrocarbon distillate of injection engine fuel characteristics.

7. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 550° F. and a U. O. P. characterization factor above about 11.3 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 250 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F., and removing corrosive acidic reaction products with-

out reducing the oxygen factor of the substantially acid-free oil to below about 175.

8. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 500° F. and a U. O. P. characterization factor above about 11.4 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 400 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F., and removing corrosive acidic reaction products without reducing the oxygen factor of the substantially acid-free oil to below about 280.

9. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 475° F. and a U. O. P. characterization factor above about 11.5 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 550 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F., and removing corrosive acidic reaction products without reducing the oxygen factor of the substantially acid-free oil to below about 385.

10. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 450° to 550° F. and a U. O. P. characterization factor above about 11.3 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, cooling the treated oil to a temperature below about 250° F., removing corrosive acidic reaction products and washing the treated oil with water without reducing the oxygen factor of the substantially acid-free oil to below about 35.

11. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 550° to 650° F. and a U. O. P. characterization factor above about 11.5 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, cooling the treated oil to a temperature below about 250° F., removing corrosive acidic reaction products and washing the treated oil with water without reducing the oxygen factor of the substantially acid-free oil to below about 35.

12. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 275° to 325° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F. while continuing the treatment with the oxygen-containing gas, and reducing the soap number and the neutralization number of the treated oil to below 0.05 and 0.25, respectively, without reducing the oxygen factor of the produced substantially soap-free and acid-free oil to below about 35.

13. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 290° to 310° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F. while continuing the treatment with the oxygen-containing gas, and reducing the soap number and the neutralization number of the treated oil to below 0.05 and 0.25, respectively, without reducing the oxygen factor of the produced substantially soap-free and acid-free oil to below about 35.

14. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an

oxygen-containing gas at a temperature within the range 250° to 350° F., in the presence of a catalyst selected from the group consisting of alkali and alkaline earth metal oil-soluble soaps, for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50 but insufficient to increase the neutralization number of the oil by more than about 15, cooling the treated oil to a temperature below about 250° F. while continuing the treatment with the oxygen-containing gas, and reducing the soap number and the neutralization number of the treated oil to below 0.05 and 0.25, respectively, without reducing the oxygen factor of the produced substantially soap-free and acid-free oil to below about 35.

15. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 250° to 350° F., in the presence of between 0.1% and 2.5% by weight of calcium naphthenate, for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50, cooling the treated oil to a temperature below about 250° F. while continuing the treatment with the oxygen-containing gas, and reducing the soap number and the neutralization number of the treated oil to below 0.02 and 0.25 respectively, without reducing the oxygen factor of the produced substantially soap-free and acid-free oil to below about 35.

16. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising preliminarily subjecting a crude petroleum distillate to a refining treatment effective to materially reduce the content of components of relatively high carbon to hydrogen ratio, to substantially completely remove asphaltic and resinous material and to produce an oil having a U. O. P. characterization factor of at least 11.15, and thereafter subjecting the said preliminarily treated distillate to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 5 but insufficient to increase the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the treated oil decreases to below about 5, removing acidic reaction products from the treated oil, and washing with water without reducing the oxygen factor of the treated substantially acid-free oil to below about 5.

17. A process of preparing an improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, comprising preliminarily subjecting a crude petroleum distillate to a refining treatment effective to materially reduce the content of components of relatively high carbon to hydrogen ratio, to substantially completely remove asphaltic and resinous material and to produce an oil having a U. O. P. characterization factor of at least 11.15, and thereafter subjecting the said preliminarily treated distillate to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than about 50 but insufficient to increase the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the treated oil decreases to below about 50, and removing acidic reaction products from the treated oil without reducing the oxygen factor thereof to below about 35, and blending the said produced substantially acid-free oil with from 2% to 20 times its volume of a clean petroleum distillate of injection engine fuel characteristics.

18. An improved injection engine fuel containing substantial proportions of chemically combined reactive oxygen, which chemically combined reactive oxygen is directly measurable in terms of oxygen factor of the said fuel, having an oxygen factor higher than about 5, a soap number no higher than 0.05 and a neutralization number no higher than about 0.25, prepared by subjecting a petroleum distillate injection engine fuel relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, having an A. S. T. M. 50% boiling point within the range 325° to 650° F. and a U. O. P. characterization factor above about 11.15 to treatment in liquid phase with an oxygen-containing gas at a temperature within the range 200° to 400° F. for a period of time sufficient to produce an oil having an oxygen factor of higher than 5 but insufficient to increase the neutralization number of the oil by more than about 15, arresting the said treatment before the oxygen factor of the produced oil decreases to below 5, and reducing the soap number and the neutralization number of the produced oil to below 0.05 and 0.25, respectively, without reducing the oxygen factor of the produced oil to below 5.

THOMAS H. SCHULTZ.
IRVING E. LEVINE.
HOMER B. WELLMAN.