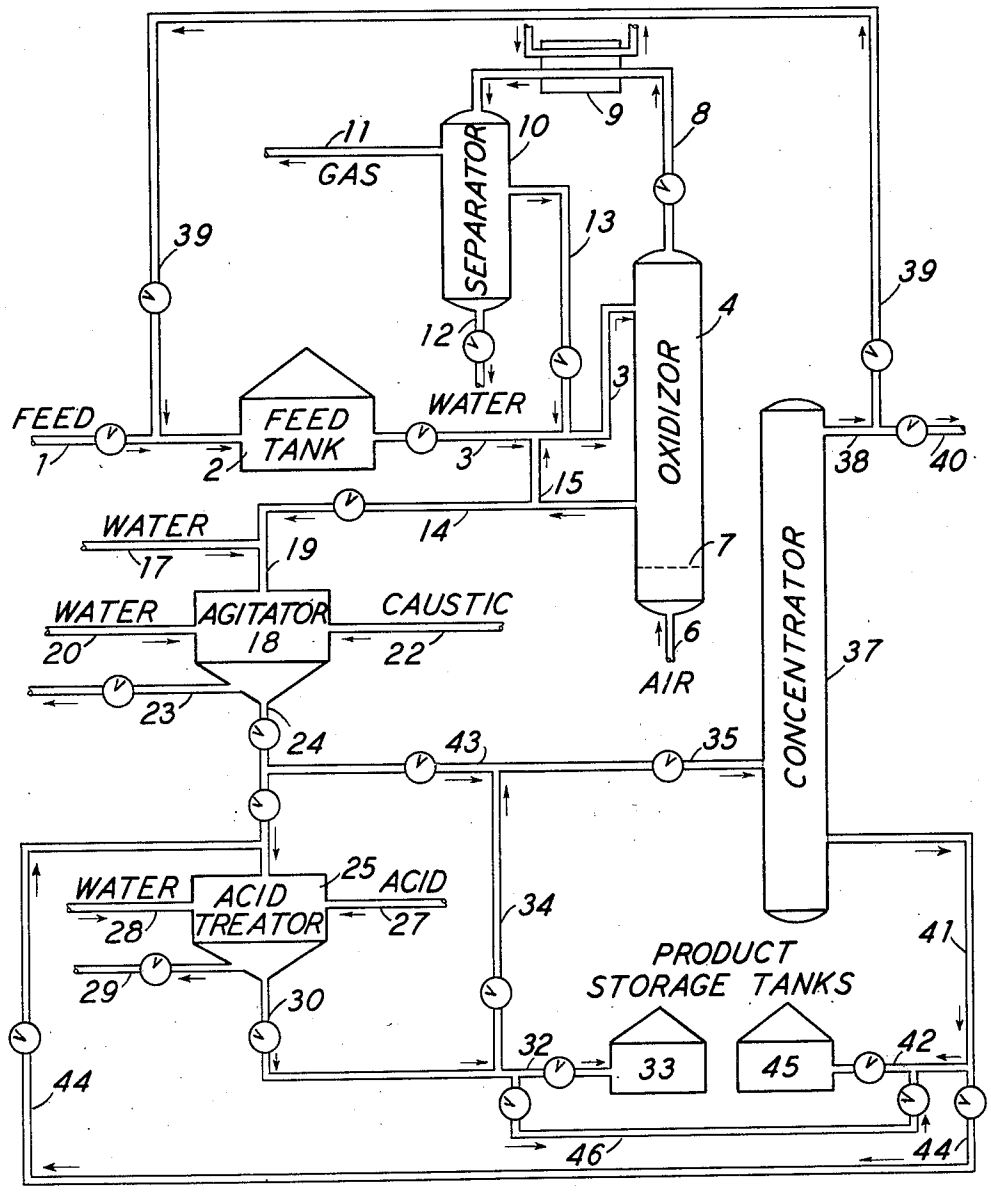
Sept. 12, 1950 G. H. DENISON, JR., ET AL 2,521,698

INJECTION ENGINE FUEL

Filed May 2, 1946



INVENTORS:

George H. Denison, Jr.

John E. Hanson

BY: J. M. Adams

W. H. Borchuding

ATTORNEY

Patented Sept. 12, 1950 2,521,698

UNITED STATES PATENT OFFICE

2,521,698

INJECTION ENGINE FUEL

George H. Denison, Jr., and John E. Hanson, Berkeley, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

Application May 2, 1946, Serial No. 666,701

15 Claims. (Cl. 196—142)

1

This invention relates to improvements in fuels for injection engines, and especially to fuels for internal combustion engines of the Diesel type, in which a liquid fuel is injected into the combustion chamber and ignited by compression; and in certain aspects relates particularly to the modification of hydrocarbon fuels employed in compression ignition motor service and the admixture or blending of such modified fuels with ordinary or special hydrocarbon fuels of the Diesel type in such a manner as to enhance the combustion characteristics for Diesel motor purposes.

In the attainment of minimum engine knocking the time interval between the instant of liquid fuel injection and 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 hydrocarbon composing the fuel. It is likewise known that it may be shortened by the addition to the fuel of various "accelerators" or "primers." Such ignition accelerators or primers are mechanically admixed with or dissolved in the fuel hydrocarbons generally in amounts between 0.1% and 10% by weight of the fuel hydrocarbon. 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 obtained are attended by adverse effects of other sorts.

In the present invention, fuels of high ignition quality as measured by decrease in delay periods are prepared by derivation from the petroleum hydrocarbons which themselves could suitably compose the usual whole Diesel fuel or from hydrocarbons more volatile than the usual whole Diesel fuel or fractions thereof. This modified fuel is derived in its simplest terms through a carefully controlled partial oxidation of said hydrocarbons under definitely controlled conditions followed by supplementary treatment of the partially oxidized oil designed to produce a composition which is not subject to deterioration in storage and is free from components adverse in their effects upon Diesel engine operation. As prepared, the fuels of the invention are low in cost, of consistently high ignition quality, permanent and stable in storage, and generally without adverse qualities from the standpoint of marketability.

The processes of this invention provide for the preliminary selection of a suitable feed stock or treatment of a synthetic or natural petroleum fuel or gasoline or kerosene distillate or ordinary

2

Diesel fuel characteristics or a portion of such a fuel by such means as will produce a suitable feed stock composed of hydrocarbons capable upon partial oxidation in the liquid phase with air or other oxygen-carrying gas of attaining an oxygen factor of at least 250, and treating said hydrocarbons with an oxygen-containing gas under such conditions as will allow it to attain said oxygen factor, without concomitant increase in neutralization number of more than about 15; treating the partially oxidized oil with a strong acidic reagent and to a subsequent caustic wash to give a highly stable non-corrosive product which may be employed as an injection engine fuel in and of itself or may be blended with one or more ordinary hydrocarbon fractions to produce a fuel of the desired high ignition and other qualities.

The character of the oil used for feed is of considerable consequence in providing a mixture of hydrocarbons capable of attaining high oxygen factors on oxidation and exhibiting a generally proportional increased cetane number value.

In general, these oils should be free from large proportions of aromatic ring structures, asphaltic and resinous materials and large quantities of natural anti-oxidants and should contain a group of relatively volatile hydrocarbons. Straight-run petroleum distillates are preferred as initial materials and such distillates preferably should be acid-treated or selectively-solvent refined before oxidation for optimum results. 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.

The oxidation step of the process is preferably carried out within the temperature range of 250° F. to 350° F. and preferably with the aid of a small amount of seed stock from the previous run. An amount of seed stock between about 0.5% and 5% is usually desirable. The oxidation is continued for a time not materially longer than is necessary to give an oil of the maximum oxygen factor attainable and also to prevent undue formation of undesirable side reaction products. In general, the oxidation step is regu-

lated to produce an oxygen factor of at least 250 and a neutralization number of not more than 15. The partially oxidized oil should not be allowed to remain at or near oxidizing temperature for any considerable length of time subsequent to the attainment of the desired oxygen factor due to the secondary reactions which continue at the expense of the desirable product. It is therefore of importance to quickly cool the oil as, for example by quenching with water to a temperature below that at which secondary reactions are rapidly taking place, namely, to a temperature below about 250° F. and preferably as low as 100° F.

It is frequently desirable to wash this partially oxidized oil with a dilute caustic solution to remove acidic substances and salts or soaps of organic acids before proceeding with the subsequent treatment. A 5% aqueous caustic solution in an amount equivalent to about 10% more than that theoretically required to effect neutralization is preferably used. A materially stronger caustic solution tends to destroy the desired partially oxidized hydrocarbons as does a substantial excess of the caustic. In some cases where acid is not formed on oxidation or is not detrimental, it is advantageous to dispense with the caustic wash and proceed with the subsequent treatment.

Further complete discussions of the steps of partial oxidation, quenching, and caustic washing a chosen feed stock as well as analytical methods for the determination of oxygen factor and neutralization number are given in U. S. Patents Nos. 2,365,220 and 2,317,968 to Shultze et al. In preferred and specific aspects, the process and products provided by our invention may be regarded as improvements on those described in said patents involving the discovery and utilization of a supplementary treatment applied to the products of the patents as initial feed stocks, whereby the high cetane number enhancement capability of the partially oxygenated compounds is substantially retained concurrently with a conversion of these compounds to a state which is more stable and characterized by an entirely or substantially reduced tendency to produce corrosion. A further feature of improvement resides in the provision of the partially oxygenated compounds in a concentrated state. Our improvement process is applicable either in conjunction with the process of Patent No. 2,365,220, wherein charging stocks corresponding to an A. S. T. M. 50% boiling point within the range 325° to 650° F. are employed, or Patent No. 2,317,968, wherein the charging stock boils within the range 200–450° F.

Pursuant to this invention, it has been found possible and highly important to treat this partially oxidized product with a strongly acidic material to form a stable, less corrosive, and more readily usable product. It has furthermore been found that the oxygen-containing cetane-improving compounds present in this partially oxidized oil and measurable in terms of oxygen factor may be successfully converted to a superior type of oxygen-containing compounds which are more stable in storage upon admixture with certain types of base fuels and which are substantially less corrosive. Furthermore, it has been discovered that this acid treatment to produce a highly stable, non-corrosive cetane-improving compound may be accomplished without effecting a substantial decrease in the cetane-improving qualities of the partially oxidized stock being treated. For instance, five per cent of the partially oxygenated hydrocarbons prepared as hereafter described, having an oxygen factor of about 800, added to an untreated waxy automotive Diesel base fuel gave a cetane increase of 7.4 numbers and five per cent of the same stock after acid treatment had an oxygen factor of about 100 and gave a cetane number increase of 5.7. The loss due to acid treating was therefore 1.7 cetane numbers or about 25% of the cetane improvement capability of the untreated partially oxidized stock. In general, it has been found that a loss in cetane improving capability of up to approximately 25% may be encountered in the acid treating step of the process. Experimental results, however, are somewhat variable and in some instances show less decrease in cetane improvement capability and in other special cases show a loss in excess of 25% by the acid treating procedure disclosed. However, the partially oxidized stock not given the treatment with an acidic reagent lacks stability and gradually loses its cetane-improving characteristics on storage while the treated stock maintains a substantially constant value. In addition, the untreated partially oxidized stock shows a high corrosivity to lead, while the acid treated stock shows very little corrosion. The lead corrosion test is carried out by immersing a lead strip ½" x 1½" x $\frac{1}{16}$" in a beaker of the sample maintained for twenty hours at about 225° F. The loss in weight of the lead strip is noted. The substantial improvement obtained as to both stability with respect to cetane number improvement and decrease in corrosivity is shown on a quantitative basis by the data on comparative experiments given in Tables I(*a*) and I(*b*). The concentrated stock used in Table I(*a*) was prepared as hereinafter described.

TABLE I(*a*)

Cetane number stability

Treatment of Concentrated Partially Oxidized Stock	Oxygen Factor	Percent Added to SCR [1]	Cetane Improvement		
			15 min.	48 hrs.	96 hrs.
None	6,240	2	12	7	6
1½ lb. 75% H_2SO_4/gal.	840	2	11	11	10

[1] SCR refers to Southern California Regular Automotive Diesel base having a cetane number of 36.

TABLE I(*b*)

Lead corrosivity

Treatment of Partially Oxidized Stock	Oxygen Factor	Per Cent Added to Untreated Automotive Waxy Base	Lead Corrosion
			Mg.
None	839	10	158
1¼ lb. of 75% H_2SO_4/gal.	141	10	7

Some of the strongly acidic materials which have been found suitable for this acid stabilization step are sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, technical dimethyl sulfate and the like. Table II shows a comparison of various acid treatments, and the products obtained thereby as to their cetane number enhancement capability. The data shows various acid treatments of a partially oxidized concentrate, the resultant product then being incorporated as an additive to a Southern California Regular Diesel (SCR) stock in the amounts noted.

The resulting fuel was allowed to stand approximately one month before testing for cetane number increase.

TABLE II

Partially Oxidized Concentrate Treated with—	Per Cent Additive in SCR [1]	Cetane No. Increase
Sulfuric acid (20%)	5	3.4
Sulfuric acid (75%)	5	8.3
Sulfuric acid (96%)	5	7.0
Hydrochloric acid (37%)	6	5.7
Phosphoric acid (85%)	5	7.0
Nitric acid (70%)	5	8.4
Dimethyl sulfate	4	6.8

[1] SCR refers to Southern California Regular Automotive Diese base having a cetane number of 36.

It has been found convenient to use sulfuric acid in this step of the process, and its use will be further described. However, many other strongly acidic substances can be substituted therefor as noted above; specific conditions of treatment may be slightly different and varied with the various acidic reagent to give optimum results.

In general, it has been found that between 0.1 and 0.75 lb. of 50% to 98% sulfuric acid per gallon of the partially oxidized unconcentrated feed stock is desirable. It has further been found that under usual operating conditions a treatment with about ¼ lb. of 75% sulfuric acid per gallon of the feed gives optimum results. A treating time of between about five and ninety minutes and especially between about fifteen and about sixty minutes is to be preferred. Treating temperatures up to 95° F. have been successfully used; however, an intermediate range of 50° F. to 85° F. is more suitable and 60° F. to 80° F. is preferable. Temperatures as high as 145° F. give serious decomposition of the active cetane number improving ingredients. When properly practiced under controlled temperature conditions, the acid treatment results in a substantial reduction in the tendency of the partially oxygenated hydrocarbons to cause corrosion, and a substantial improvement of their stability as to their cetane number improving quality without substantial decrease in the numerical value thereof. This change is attributed to a change in the constitution of the oxygenated compounds which it has been discovered results in and may be measured by decrease in oxygen factor. Thus, it has been ascertained that when temperature is controlled as above indicated, the reduction in the value of the oxygen factor serves as a criterion for the maintenance and attainment of optimum conditions for the acid treatment. Hence, conditions of acid treatment are preferably adjusted to give a reduction of the oxygen factor from 250 or above to 15% to 20% or less of the original value. In general, it has been observed that the lower the oxygen factor after acid treatment of the partially oxidized oil the more stable and less corrosive the acid treated product. It has further been found that the partially oxidized oil may be conveniently treated with the sulfuric acid in a batchwise manner. For example, it has been found that the temperature may be more readily controlled to the desired value by adding the total sulfuric acid employed in four dumps with a cold water wash between each dump. The number of dumps may be increased or decreased as desired or even combined into one in some cases in accordance with this invention. The effect of varying the

conditions under which acid treatment is accomplished is shown by the data of Table III. Data was secured by acid treating the partially oxidized stock using ¼ lb. of acid per gallon. The product was tested by adding 10% of the acid treated stock to a Southern California Regular Diesel base stock having a cetane number value of 35. Cetane numbers were determined seventy-two hours after blending.

TABLE III

Acid Strength	Treating Time, min.	Treating Temp., °F.	Average Cetane No. Rise
Per cent			
75	15–60	50–80	9
75	15–60	140	1
75	1	50–80	3

The acid treated oil is preferably washed with water after the last acid treatment to remove excess acid, is then washed with dilute caustic until neutral, and finally with water till salt and caustic free. It is preferable to use a 10% excess of 5% aqueous caustic over that required for neutralization for this wash. Stronger caustic destroys the active oxygen components present and an appreciably larger excess of caustic is also detrimental to the final product.

When the oil feed stock chosen for oxidation is suitable for use as a Diesel fuel, the product is now an improved Diesel fuel and is ready for use. If, however, the oil feed stock selected is not a suitable Diesel fuel, as for instance by reason of its low boiling range, or if the object is to produce a blending agent which may be added to a Diesel fuel stock to increase the cetane number, the acid treated oil may be added to a base stock in an amount to produce a fuel having the desired cetane number.

It is frequently desirable, however, to utilize this product as a blending agent in a more concentrated form, and in such cases the active cetane-improving component is concentrated before blending. The concentration step may be utilized either prior to or subsequent to the treatment with acid. Any method which is capable of concentrating the desired oxidized hydrocarbon is adaptable to the practice of this modification of the process of this invention. For example, the oxidized hydrocarbons may be concentrated by distillation, or by other suitable means, for example, by solvent extraction or by adsorption fractionation. In many cases it will be found preferable to concentrate by distillation, and this method is illustrated and more fully described, although it is to be understood other methods are equally applicable. Ordinarily, it is preferable to concentrate this material by removing the lower boiling unoxidized hydrocarbons from the mixture. This distillation is preferably carried out until only about 20% of the original volume remains in the still; however, this residue may vary between about 5% and 40% of the original charge, depending on conditions of previous treatment and expected uses. The 80% more or less removed contains substantially only inert or non-cetane-improving hydrocarbons and may be recycled to the oxidation step of the process or may be otherwise utilized or discarded. The bottoms remaining in the still may suitably contain of the order of 40% of the initially partially oxidized oil and contains in highly concentrated

conditions the active oxygen-containing, cetane-improving compounds, desirably at least 45%, and especially 50% of cetane-improving compounds. In general, after the acid treatment described above and the concentration step of the process, the oxidized concentrated oil will have an oxygen factor of not greater than 600, and preferably less than 300. It has been found that this concentration by distillation may best be carried on at a subatmospheric pressure of between 10 mm. of mercury and atmospheric pressure and especially at about 30 mm. pressure. The optimum pressure is determined by the properties of the charging stock being concentrated. In general, a higher pressure is usable with a lighter charging stock. The temperature desirably is maintained below 350° F., preferably below 250° F. and especially of the order of 200° F.

Under some conditions of operation, it is preferable to concentrate the cetane-improving components of the partially oxidized oil before the acid treatment. In this case the cetane-improving compounds are concentrated as before by subjection of the partially oxidized stock prior to the acid treatment, to distillation, solvent extraction, or adsorbent fractionation. When distillation is used, fractionation preferably is carried out in the manner and to the extent outlined above. The more volatile component which is removed can be recirculated to the oxidation step of the process or discarded. The bottoms remaining in the still contain oxygenated compounds and exhibit an increased oxygen factor of at least 1000, preferably about 3000 to 7000 or even to 15,000. Concentration by distillation is carried out under conditions of temperature and pressure similar to those outlined above for concentration of acid treated oil.

The concentrated product is then acid treated as before, except a correspondingly greater amount of acid per gallon of stock is used to give a final product having an oxygen factor not greater than 20% of the oxygen factor of the concentrate, preferably below 600, and more suitably less than about 300.

Although a distinct two-step process of oxidation and acid treatment has been described and is regarded as preferable, it is also considered within the scope of this invention to effect the partial oxidation and acid treatment concurrently in the same treating vessel and consequently produce the desired cetane-improving product in one step, namely, partial oxidation of the charging stock in the presence of the acid to give the above-described product.

The acid treated concentrated oxidized oil produced either by acid treatment of the unconcentrated stock followed by distillation or by acid treatment of the concentrated stock may be used as a cetane-improving additive in ordinary Diesel fuel in amounts between about 0.2% to 25% of the base fuel desirably between about 1% and 15%, and especially about 2% to 8% of the base fuel.

The Diesel fuels of this invention may also contain additional additives in some cases. For example, ordinary accelerators or primers may be added to the finished product as well as antioxidants when desirable.

In one mode of operation, the invention may be carried out as exemplified in the flow diagram of the appended drawing. Selected hydrocarbons adapted as previously described for the preparation of the improved injection engine fuel of this invention are fed via valve controlled line 1 to feed tank 2. These oils are then passed via valve controlled line 3 to oxidizer 4 where air enters via line 6, is dispersed by porous plate 7 and contacts the body of oil in the oxidizer. Oxidizer 4 is maintained at optimum oxidizing conditions to give controlled aeration of oil; residual gas and volatile hydrocarbon products leave the oxidizer via valve controlled line 8 through a cooling and condensing unit 9 and enter separator 10 where the mixture is separated. Gas and uncondensed vapors are removed via line 11. A water layer is removed via valve controlled line 12 and a hydrocarbon layer is removed at an intermediate point and recirculated to oxidizer 4 via valve controlled lines 13 and 3. It is sometimes advantageous to recirculate the main body of oil in oxidizer 4 by passing oil via a closed circuit including valve controlled lines 14, 15 and 3 (and suitable pumping means not illustrated). Or in some instances two or more oxidizers in series may be substituted for oxidizer 4 in which case the oil is circulated from the first oxidizer to subsequent oxidizers and is withdrawn from the last oxidizer in the series. When the oil has been treated to the degree desired as measured by the oxygen factor and neutralization number of samples withdrawn at suitable intervals, the treated oil is withdrawn from oxidizer 4 via valve controlled line 14, is rapidly cooled with water from line 17, and the cooled mixture is fed to agitator 18 via line 19. The partially oxidized oil is washed with water from line 20 and then with dilute aqueous caustic solution from line 22. Spent aqueous solutions are withdrawn via valve controlled line 23. The partially oxidized caustic-scrubbed oil may then be passed via valve controlled line 24 to acid treator 25 where it is treated with a strong acid from line 27 under the conditions previously described, and then with water from line 28. Spent aqueous layer is removed via valve controlled line 29. The acid treated oil may then be fed via valve controlled lines 30 and 32 to storage tank 33. If a more concentrated additive is desired, the acid-treated oil may be fed via valve controlled lines 34 and 35 to a concentrator such as fractionating or distilling column 37 where the relatively volatile inert components are removed via line 38 and valve controlled lines 39 and 1 to feed tank 2 for recirculation through the system or are removed from the system via valve controlled line 40. Column 37 may be provided with conventional heating and refluxing means not illustrated. Concentrated, acid-treated oil constituting the desired cetane-improving product, is removed via line 41 and valve controlled line 42 to storage tank 45.

Alternatively, the partially oxidized hydrocarbons may be concentrated prior to the acid treatment. In the practice of this embodiment of the invention, the caustic washed partially oxidized oil may be passed from agitator 18 via valve controlled lines 24, 43 and 35 to concentrator 37 where the volatile components are removed via line 38 as before. The concentrated oxygen-containing fraction is then passed via line 41 valve controlled lines 44 and 24 to acid treator 25 where this concentrated oxygen-containing product is treated with acid as before but with increased quantities of acid corresponding to the increase in concentration of the feed. The concentrated, acid-treated product is then passed via valve controlled lines 30, 32, 46 and 42 to storage tank 45.

The practice of the invention is further shown by the following specific examples:

Example 1.—700 cc. of Stoddard distillate, which after washing with one-half pound of 96% sulfuric acid per gallon, was relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds, had a gravity of 46.4° API, boiled within the range of 310° F. and 364° F., and had a cetane number of about 35, was oxidized in a treator similar to oxidizer **4** shown in Figure 1.

In this oxidation, the oil plus 18 cc. of seed stock from a previous run was air-blown for three hours at a temperature of about 300° F. and at a rate of two volumes of air per volume of oil per minute. The partially oxidized oil from this operation had an oxygen factor of 801 and cetane number of 77. This product was washed with a ten per cent excess of 10% aqueous caustic to give a product having a neutralization number of 1. This neutralized, partially oxidized oil was then treated with one-quarter pound of 75% sulfuric acid per gallon of oil added in five dumps over a period of fifteen minutes at a temperature of about 75° F. This partially oxidized product had an oxygen factor of 98, a neutralization number of 0.04, and a cetane number of 65.5, and constituted a highly desirable Diesel motor fuel for use as such or in a blend with other lower quality components. For example, when 5% of this partially oxidized acid treated product was added to an untreated automotive waxy Diesel fuel base having a cetane number of 42, the cetane number of the blended fuel was raised to 47.7.

The foregoing process example covering oxidation and acid treating steps illustrates the practice of the invention by a procedure wherein a concentrating step is not employed.

Example 2.—The acid treated, partially oxidized oil produced in Example 1 is distilled at 5 mm. of mercury pressure and 130° F. until 80% of its volume has been removed. The vaporized portion had an oxygen factor of 13 and a neutralization number of less than 0.005, while the concentrate remaining in the still had an oxygen factor of 670 and a neutralization number of 0.033. Three per cent of this concentrated product was added to on untreated waxy automotive Diesel base fuel boiling within the range of 340° F. to 576° F. and having a cetane number of 41.1. The cetane number of this blended fuel after sixteen days of storage was 52.4.

Example 3.—700 cc. of the same acid washed Stoddard distillate as used in Example 1 was fed to the oxidizing reactor. 18 cc. of seed stock was added and the mixture air-blown for three hours at 300° F. using an air rate of two volumes per volume of oil per minute. The resulting product had an oxygen factor of 1175 and neutralization number of 11. This partially oxidized product was treated with one-quarter pound of 75% sulfuric acid per gallon for fifteen minutes at 70° F. The acid treated product was washed with 5% caustic and water and had an oxygen factor of 164 and a neutralization number of 0.01. The washed, acid treated product was distilled at 5 mm. of mercury pressure and 122° F. until twenty per cent of the original volume remained as a residue or concentrate. This remaining concentrate had an oxygen factor of 740 and a neutralization number of 0.1. Three per cent of this concentrated product was blended with an untreated waxy automotive Diesel base having a cetane number of 41.1. After sixteen days' storage this blend showed a cetane number of 50.9 or an increase in cetane number of 9.8.

Example 4.—A Stoddard distillate similar to that used in Example 1 was oxidized and caustic washed as outlined in Example 1. 17% of this partially oxidized product was blended with an automotive Diesel fuel boiling within the range of 308° F. to 578° F. and having a chart cetane number of 42. This blended stock having an oxygen factor of 153 was then treated with one-quarter pound of 93% acid per gallon of stock at about 70° F. The finished stock had an oxygen factor of 2.2 and a cetane number of 50.5.

Example 5.—A Stoddard distillate similar to that used in Example 1 was air-blown and caustic washed as in Example 1 and thereafter exhibited an oxygen factor of 839 and a neutralization number of .12. This partially oxidized product was distilled at 30 mm. pressure and a temperature under 200° F. to separate the higher boiling fraction as a concentrate constituting about 12.5% of the original liquid volume. Two per cent of this concentrated product having an oxygen factor of 6240 was then blended in a Southern California Regular refined distillate boiling within the range of 388° F. to 656° F. and having a cetane number of 41. After forty-eight hours' storage, this blend had a cetane number of 48.2.

Example 6.—A Stoddard distillate similar to that employed in Example 1 was oxidized, neutralized, and concentrated as in Example 5. One portion of the concentrate was treated with one-quarter pound of 75% sulfuric acid per gallon at 77° F. for fifteen minutes and a second portion was treated with one and one-half pounds of 75% sulfuric acid per gallon at 77° F. for twenty minutes. The two products had oxygen factors of 3920 and 840, respectively. Two per cent of each of these products was added to an automotive base fuel having a cetane number of 40.9. After ninety-six hours of storage the blended fuels had cetane numbers of 49.1 and 50.8, respectively.

We claim:

1. A process of preparing an improved injection engine fuel which comprises subjecting a petroleum distillate which is predominantly saturated hydrocarbons and is relatively free of asphaltic and resinous materials to treatment at 200 to 400° F. in liquid phase with an oxygen-containing gas to produce a partially oxygenated oil having substantial proportions of chemically combined reactive oxygen directly measurable in terms of the oxygen factor of the said fuel and exhibiting a generally proportional increased cetane number value, and contacting said resultant oxygenated oil with a strongly acidic reagent at a sufficiently low temperature of below about 150° F. and short contact time below about 90 minutes to retain a high cetane number value of the resulting oxygenated oil and with a sufficient amount of said reagent to convert a substantial proportion of said oxygenated oil to a more stable and less corrosion-producing oxygenated oil having a reduced oxygen factor, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

2. The process of claim 1 wherein said petroleum distillate has an ASTM 50% boiling point within the range 325° to 650° F.

3. The process of claim 1 wherein said petroleum distillate boils within the range 200° to 450° F.

4. The process of claim 1 wherein the acid con-

tacting step is carried out at a temperature below 95° F. and with at least 0.1 pound of acidic reagent per gallon of partially oxygenated oil.

5. The process of claim 1 wherein said acidic reagent is a relatively concentrated aqueous solution of sulfuric acid.

6. A process of preparing an improved injection engine fuel which comprises subjecting a petroleum distillate relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds to treatment at 200 to 400° F. in liquid phase with an oxygen-containing gas to produce a partially oxygenated oil having substantial proportions of chemically combined reactive oxygen directly measurable in terms of the oxygen factor of the said fuel and exhibiting a generally proportional increased cetane number value, and converting a substantial proportion of the chemically reactive oxygen-containing components of said oxygenated oil to oxygenated compounds having a reduced sensitivity to the oxygen factor test by contacting said partially oxygenated oil with a strongly acidic reagent under mild conditions including a temperature of below 95° F. and a relatively short contact time of less than about 90 minutes whereby oxygen factor sensitive oxygenated compounds are converted to more stable and less corrosion-producing oxygen factor insensitive oxygenated compounds which are effective to improve the cetane number of the fuel, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

7. A process of preparing an improved injection engine fuel which comprises the steps of subjecting a petroleum distillate to a liquid phase oxidation treatment with an oxygen-containing gas at a temperature within the range of 200° F. to 400° F. and for a period of time sufficient to produce an oil having an oxygen factor higher than about 250, concentrating said oxidized oil by means of fractional distillation at a temperature below 350° F. at a pressure between 10 mm. of mercury and atmospheric and for a length of time sufficient to volatilize between 60 and 95% of said oxidized oil, thereby producing a residue having an oxygen factor of at least 1000, and contacting said residue with between 0.1 and 1 pound of a strongly acidic reagent per gallon of said residue at a temperature below about 95° F. for a relatively short time of less than about 90 minutes to reduce the oxygen factor of said residue to less than about 20% of its original value, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

8. A process of preparing a relatively stable cetane-improving oxygenated oil which comprises contacting partially oxygenated hydrocarbon oil containing chemically combined reactive oxygen in sufficient proportions to give an oxygen factor of at least 250 and having a high cetane number value with a strongly acidic reagent at a temperature below 150° F. for a period less than 90 minutes to convert a substantial proportion of said partially oxygenated hydrocarbon oil to a relatively stable oxygenated oil of substantially reduced sensitivity to the oxygen factor test and having a high cetane number value, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

9. A process of producing an improved Diesel fuel component from a mixture including non-oxygenated and partially oxygenated hydrocarbon compounds containing reactive oxygen measurable in terms of the oxygen factor test and exhibiting a correspondingly high cetane number value which comprises treating said mixture with a concentrated aqueous solution of sulfuric acid under mild conditions including a temperature of below 150° F. and a relatively short contact time of less than about 90 minutes to convert said original oxygenated compounds to more stable and less corrosion-producing oxygenated compounds having a high cetane number and a substantially reduced oxygen factor, and separating the acid treated partially oxygenated from the non-oxygenated compounds present in the mixture to produce a concentrate of the relatively stable partially oxygenated hydrocarbons.

10. The process of claim 9 wherein in the acid contacting step there is used a small amount of acid less than 1 pound per gallon of said mixture of non-oxygenated and partially oxygenated hydrocarbon compounds.

11. A process of producing an improved Diesel fuel component from a mixture containing non-oxygenated and oxygenated hydrocarbon compounds containing reactive oxygen measurable in terms of the oxygen factor test and exhibiting a correspondingly high cetane number value which comprises separating non-oxygenated hydrocarbons from said oxygenated hydrocarbons to produce a concentrate of the latter, and contacting said concentrate with a strongly acidic reagent under mild conditions including a temperature of below 150° F. and a relatively short contact time of less than about 90 minutes to convert said oxygenated hydrocarbons to more stable oxygenated hydrocarbons having a high cetane number value and a reduced oxygen factor, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

12. A process of preparing an improved injection fuel which comprises treating a petroleum distillate with an oxygen-containing gas at a temperature within the range of 250° F. to 350° F. and for a period of time sufficient to produce a partially oxidized oil having an oxygen factor higher than about 250, and contacting said partially oxidized oil at a temperature below about 95° F. with a strongly acidic reagent for a relatively short time of less than about 90 minutes to reduce the oxygen factor of said oil to below about 20% of its original value, whereby the product has a relatively high cetane number and is relatively stable, said strongly acidic reagent being selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid and hydrochloric acid.

13. A process of preparing an improved injection fuel which comprises the steps of subjecting a petroleum distillate boiling within the range 200° F. to 450° F. and relatively free from asphaltic and resinous materials and from large proportions of aromatic ring compounds to a liquid phase oxidation treatment with an oxygen-containing gas at a temperature within the range of 200° F. to 400° F. and for a period of time sufficient to produce an oil having an oxygen factor higher than about 250, contacting the resulting oxygenated oil with 50 to 90% sulfuric acid in an amount of 0.1 to 0.75 pound of said acid per gallon of said oxygenated oil at a temperature of 50 to 85° F. and for a period of less than 90 minutes, thereby producing a more stable and less cor-

rosion-producing oxygenated oil having a substantially lowered oxygen factor, treating said oxygenated oil with controlled amounts of weak caustic solution to preferentially remove acidic material, and concentrating said caustic-treated oxygenated oil by means of fractional distillation at a temperature below 350° F. at a pressure between 10 mm. of mercury and atmospheric and for a length of time sufficient to volatilize between 60 and 95% of said oxygenated oil whereby there is obtained a concentrate of said relatively stable cetane-improving oxygenated oil.

14. A Diesel type motor fuel component comprising as the active ingredient a liquid oxygenated hydrocarbon conversion product of treatment of partially oxygenated hydrocarbons containing chemically combined reactive oxygen sufficient to give a relatively high oxygen factor and having a high cetane number with a strongly acidic reagent selected from the group consisting of sulfuric, nitric, phosphoric and hydrochloric acids under mild conditions of a low temperature below about 150° F. and a short contact time of less than about 90 minutes, said produce being relatively stable, relatively non-corrosive, soluble in hydrocarbons in the Diesel fuel range and having a relatively low oxygen factor and a high cetane number.

15. An improved Diesel type motor fuel comprising a solution in hydrocarbons within the

Diesel fuel boiling range having a relatively low cetane number, of a mildly treated acid conversion product of a mixture of oxygenated hydrocarbons containing reactive oxygen measurable in terms of the oxygen factor test and having a correspondingly high cetane number value, the active cetane-improving portion of said conversion product being relatively stable and soluble in hydrocarbons in the Diesel fuel range and having an oxygen factor below 300, said mild acid treatment being at a low temperature of less than 150° F. and a short contact time of less than about 90 minutes and with a strongly acidic reagent selected from the group consisting of sulfuric, nitric, phosphoric and hydrochloric acids.

GEORGE H. DENISON, JR.
JOHN E. HANSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,044,014	Penniman	June 16, 1936
2,176,655	Penniman	Oct. 17, 1939
2,213,407	Pfirrmann	Sept. 3, 1940
2,317,968	Schultz et al.	Apr. 27, 1943
2,365,220	Schultz et al.	Dec. 19, 1944
2,390,296	Gilbert	Dec. 4, 1945